

**THE EXTRACTION OF VANADIUM AND NICKEL FROM
PETROLEUM COKES.**

by

**CARLOS ENRIQUE DAVILA ARMAS
BSc(Eng), ARSM.**

A thesis submitted for the degree of Doctor of Philosophy of
the University of London and for the Diploma of Membership of
the Imperial College of Science and Technology.

February 1988

Department of Mineral
Resources Engineering,
Royal School of Mines,
Imperial College of Science and
Technology,
University of London.

ABSTRACT.

The recovery of metal values from Venezuelan petroleum cokes produced by the Flexicoking and Delayed coking processes has been investigated by a hydrometallurgical technique and by a vapour transport process. Most of the work was conducted using Flexicoke.

The extraction of vanadium and nickel from Flexicoke and Delayed coke by leaching with a variety of inorganic and organic reagents has been investigated. Extractions of vanadium were low with as-received Flexicoke. Grinding of the coke produced quite good vanadium extractions; the effect of temperature, acid concentration, particle size of coke and agitation speed on vanadium extraction and extraction rate were investigated. Nickel extractions were low and hardly affected by changes in temperature, acid concentration or coke particle size. Vanadium and nickel recoveries from Delayed coke were negligible.

Laboratory-scale experiments have been carried out in which a fixed bed or fluidized bed of coke was heated to the required temperature and reacted with hydrogen chloride gas. A condensate consisting mainly of vanadium, nickel and iron chlorides was obtained in the cooler parts of the reactor. Metal recoveries have been investigated using two level factorial designs with the following variables: temperature, partial pressures of hydrogen chloride and water vapour, time, coke particle size and gas flow rate. Vanadium and nickel recoveries greater than 85% and 80%, respectively, were obtained, resulting in a clean coke suitable for anode production. The kinetics of vanadium and nickel extraction were also investigated. The rate controlling step for vanadium extraction was found to change from chemical control to product diffusion control as the HCl partial pressure is increased and as the temperature is decreased. The extraction

and extraction rate are increased by reducing the particle size. Vanadium extraction fits a pseudo-first order rate equation. Nickel extraction is chemically controlled under the conditions studied. Both vanadium and nickel extraction rates were found to be first order with respect to HCl concentration.

An spectrophotometric investigation of vanadium (V) and vanadium (IV) complexes in sulphuric acid has been carried out. Stepwise stability constants for the $\text{VO}_2^+ \text{-HSO}_4^-$ system in the sulphuric acid concentration range 0-13 M and for the $\text{VO}^{2+} \text{-SO}_4^{2-}$ in the sulphuric acid concentration range 0-6 M are given.

CONTENTS.

	Page
Abstract	2
Contents	4
List of Figures	7
List of Tables	13
List of Plates	17
Introduction	18
 Chapter 1 Literature Survey.	
1.1 Metals in petroleum	20
1.1.1 Introduction	20
1.1.2 Occurrence and concentration of metals in petroleum	20
1.1.2 a) Metalloporphyrins.	23
1.1.2 b) Non-porphyrin metals	24
1.1.3. Origin of metals in petroleum.	26
1.1.4 Consequences of the presence of metals in petroleum.	31
1.2 Upgrading processes used for high metal content petroleum.	32
1.2.1 Introduction.	32
1.2.2 Coking processes.	34
1.2.2 a) Delayed coking process.	34
1.2.2 b) Flexicoking process.	37
1.3 Petroleum coke and its uses	41
1.3.1 Petroleum cokes.	41
1.3.2 Metal extraction from petroleum residues	43
1.3.2 a) Metal extraction from fly ashes.	43
1.3.2 b) Metal extraction from petroleum cokes	56
1.3.3 Other uses of petroleum cokes.	62
1.4 The segregation process.	66
1.4.1 Introduction	66
1.4.2 The production of the chloridizing gases.	68

1.4.3	Formation of the nickel chloride species.	69
1.4.4	Reduction of the nickel chloride.	73
1.4.5	Chlorination of vanadium ores	74

Chapter 2 Experimental procedure.

2.1	Materials.	77
2.2	Elemental analysis of the cokes	79
2.3	Basic coke preparation.	80
2.4	Leaching experiments	80
2.5	Coke dissolution experiments	83
2.6	Atomic absorption spectrophotometry	83
2.7	Thermogravimetric analysis	85
2.8	Vapour transport experiments	85
2.9	X-ray fluorescence spectrometry	91
2.10	Electron microscopy work	92
2.11	X-ray diffraction.	93
2.12	Chloride analysis	93
2.13	Chlorine analysis	94
2.14	Specific surface area measurements.	94
2.15	Solubility experiments	95
2.16	Gas chromatography	95

Chapter 3 Properties of the cokes. 96

Chapter 4 Hydrometallurgy experiments Results and Discussion

4.1	Leaching of as-received Flexicoke.	102
4.2	Leaching of ground Flexicoke	106
4.2.1	Effect of temperature	106
4.2.2	Effect of acid concentration	111
4.2.3	Effect of agitation speed	117
4.2.4	Effect of particle size	117
4.3	Leaching of Delayed coke	118

**Chapter 5 Vapour transport experiments.
Results and Discussion.**

5.1	Thermodynamic study.	123
5.2	The chlorides and oxychlorides of vanadium.	131
5.3	Fixed bed vapour transport experiments.	133
5.4	Fluidized bed vapour transport experiments.	156
5.5	Vapour transport experiments with Delayed coke.	185

Chapter 6 Conclusions. 187

Appendix A Spectrophotometric studies of vanadium (V) and vanadium(IV) complexes in sulphuric acid.

A1	Introduction	192
A2	Experimental	196
A3	Results.	
A3.1	Vanadium (V)-H ₂ SO ₄ system.	197
A3.2	Vanadium (IV)-H ₂ SO ₄ system.	209
A3.2 a)	The VO ²⁺ -SO ₄ ²⁻ system.	213
A3.2 b)	The VO ²⁺ -HSO ₄ ⁻ system.	216
A4	Discussion.	216

Appendix B Two phase Fluidized bed model. 219

Appendix C List of symbols. 228

Appendix D Data Tables. 230

References	239
Suggestions for future work	254
Acknowledgements	255

LIST OF FIGURES.

Chapter 1.

- Figure 1.1 Various vanadyl porphyrin structures.
- Figure 1.2 Complexes of tetradentate ligands.
- Figure 1.3 Proposed sequence for the formation of vanadyl porphyrins from chlorophyll- α .
- Figure 1.4 Delayed coking process flow diagram.
- Figure 1.5 Flexicoking process flow diagram.
- Figure 1.6 Flow diagram of the Canadian Petrofina process.
- Figure 1.7 Effect of ashing temperature on the metal recovery from Canadian Delayed coke fly ash.
- Figure 1.8 Several treatment flow sheets for metal recovery from Canadian Delayed coke fly ash.
- Figure 1.9 Flow sheet for the recovery of vanadium and nickel from fly ash.
- Figure 1.10 Vanadium extraction from Canadian Flexicoke.
- Figure 1.11 Nickel extraction from Canadian Flexicoke.
- Figure 1.12 Metal extractions from acid leaching of Canadian Flexicoke for 2 hours, as a function of temperature.
- Figure 1.13 Equilibrium diagrams for Fe-H₂-HCl and Ni-H₂-HCl.
- Figure 1.14. Equilibrium partial pressure of metal chlorides over their oxides and with $p^2\text{HCl}/p\text{H}_2\text{O}$ ratio set by the salt-silica-water vapour equilibrium.
- Figure 1.15 Equilibrium diagrams of Ni-H₂-HCl system.

Figure 1.16 Preparation of elemental vanadium by chloride metallurgy.

Chapter 2.

Figure 2.1 Schematic diagram of leaching apparatus.

Figure 2.2 Schematic diagram of the fixed bed apparatus.

Figure 2.3 Schematic diagram of the fluidized bed apparatus.

Figure 2.4 Temperature profile in the horizontal tube furnace.

Figure 2.5 Temperature profile in the fluidized bed furnace.

Chapter 3.

Figure 3.1 Particle size distribution of as-received Flexicoke.

Figure 3.2 Particle size distribution of as-received Delayed coke.

Chapter 4.

Figure 4.1 Effect of leachant temperature on the vanadium extraction from as-received Flexicoke.

Figure 4.2 Effect of various leachants on the vanadium extraction from as-received Flexicoke.

Figure 4.3 Effect of leaching temperature on the vanadium extraction from ground Flexicoke.

Figure 4.4 Effect of leaching temperature on the kinetics of vanadium extraction from Flexicoke.

Figure 4.5 Arrhenius plot for vanadium extraction from ground Flexicoke.

- Figure 4.6 Effect of sulphuric acid concentration on the vanadium extraction from ground Flexicoke
- Figure 4.7 Effect of acid concentration on the rate of vanadium extraction from ground Flexicoke.
- Figure 4.8 Distribution of complexes for the VO^{2+} - SO_4^{2-} system as a function of the sulphuric acid concentration.
- Figure 4.9 Vanadium extraction rate from Flexicoke versus the mole fraction of the VOSO_4 complex.
- Figure 4.10 Effect of sulphuric acid concentration on the solubility of vanadium (V) and vanadium (IV).
- Figure 4.11 Effect of agitation speed on the vanadium extraction from leaching $-53\mu\text{m}$ ground Flexicoke.
- Figure 4.12 Effect of particle size on the vanadium extraction from ground Flexicoke.
- Figure 4.13 Plot of the vanadium extraction rate from the shrinking core model versus the inverse of the square of the average particle radius.

Chapter 5.

- Figure 5.1 Standard free energies of formation of some vanadium and nickel oxides and sulphides as a function of temperature.
- Figure 5.2 Standard free energies of formation of some vanadium chlorides and oxychlorides and nickel chloride as a function of temperature.
- Figure 5.3 Standard free energies of formation for some reactions of interest in the vanadium oxide-hydrogen chloride system as a function of temperature.

- Figure 5.4 Standard free energies of formation for reactions between nickel oxide and sulphides and hydrogen chloride as a function of temperature.
- Figure 5.5 DTA/DTG/TG analysis of Flexicoke in nitrogen.
- Figure 5.6 DTA/DTG/TG analysis of the VCl_4 condensate.
- Figure 5.7 DTA/DTG/TG analysis of the VCl_3 condensate.
- Figure 5.8 Effect of temperature, HCl partial pressure and gas flow rate on the vanadium extraction in factorial design 3.
- Figure 5.9 Effect of temperature, HCl partial pressure and gas flow rate on the nickel extraction in factorial design 3.
- Figure 5.10 Effect of HCl partial pressure on the activation energy for vanadium extraction between 900° and 1000°C.
- Figure 5.11 Arrhenius plot for vanadium extraction at two different HCl partial pressures from as-received Flexicoke.
- Figure 5.12 Effect of temperature on the vanadium extraction from as-received Flexicoke with pure HCl.
- Figure 5.13 Effect of temperature on the vanadium extraction from as-received Flexicoke at a HCl partial pressure of 0.25.
- Figure 5.14 Effect of particle size on the vanadium extraction from Flexicoke.
- Figure 5.15 Effect of HCl partial pressure on the vanadium extraction from as-received Flexicoke.
- Figure 5.16 Effect of HCl partial pressure on the vanadium extraction from -90+75 μm ground Flexicoke.

- Figure 5.17 Effect of HCl partial pressure on the vanadium extraction from as-received and -90+75 μ m ground Flexicoke.
- Figure 5.18 Effect of temperature on the nickel extraction from as-received Flexicoke with pure HCl.
- Figure 5.19 Effect of temperature on the nickel extraction from as-received Flexicoke with HCl partial pressure of 0.25.
- Figure 5.20 Arrhenius plot for nickel extraction at two HCl partial pressures.
- Figure 5.21 Effect of HCl partial pressure on the nickel extraction from as-received Flexicoke.
- Figure 5.22 Effect of HCl partial pressure on the nickel extraction from -90+75 μ m ground Flexicoke.
- Figure 5.23 Effect of HCl partial pressure on the rate of nickel extraction from as-received and ground Flexicoke.
- Figure 5.24 Effect of flow rate on the induction time for nickel extraction.
- Figure 5.25 Effect of flow rate on the nickel extraction from as-received Flexicoke
- Figure 5.26 Effect of coke particle size on the nickel extraction from Flexicoke
- Figure 5.27 Change in specific area of Flexicoke with time.
- Figure 5.28 Nickel radial distribution in as-received Flexicoke.
- Figure 5.29 Sulphur radial distribution in as-received Flexicoke.
- Figure 5.30 Vanadium radial distribution in as-received Flexicoke.

Figure 5.31 Vanadium radial distribution in as-received Flexicoke after 90 minutes of reaction.

Appendix A.

- Figure A1 Proportion of H_2SO_4 molecules, HSO_4^- and SO_4^{2-} ions in aqueous sulphuric acid.
- Figure A2 UV spectra for vanadium (V) solutions at various sulphuric acid concentrations.
- Figure A3 UV spectra for vanadium (V) solution in 1M Na_2SO_4 and at various sulphuric acid concentrations.
- Figure A4 Effect of the sulphuric acid concentration on the molar absorption coefficient for the $\text{VO}_2^+-\text{H}_2\text{SO}_4$ system.
- Figure A5 Plot of $1/(\epsilon^\lambda - \epsilon_0^\lambda)$ versus $1/[\text{HSO}_4^-]$ to determine K_1 for the $\text{VO}_2^+-\text{H}_2\text{SO}_4$ system.
- Figure A6 Plot of ϵ^λ versus the RHS of equation A10 for determining K_2 for the $\text{VO}_2^+-\text{H}_2\text{SO}_4$ system.
- Figure A7 Stability field diagram for the vanadium (V) complexes formed in aqueous sulphuric acid solutions.
- Figure A8 Distribution diagram for the vanadium (V) complexes formed in aqueous sulphuric acid solutions.
- Figure A9 UV spectra for vanadium (IV) solutions at various sulphuric acid concentrations.
- Figure A10 UV spectra for vanadium (IV) solution in 1M Na_2SO_4 and at various sulphuric acid concentrations.

Figure A11 Plot of the molar absorption coefficient versus the sulphuric acid concentration, for the VO^{2+} - H_2SO_4 system.

Figure A12 Stability field diagram for the complexes formed in the VO^{2+} - SO_4^{2-} system.

Figure A13 Distribution diagram for the complexes formed in the VO^{2+} - SO_4^{2-} system.

Appendix B.

Figure B1 HCl concentration profiles in the bubble phase.

Figure B2 HCl concentration profiles in the emulsion phase.

LIST OF TABLES.

Chapter 1.

Table 1.1 Typical concentration range of the principal trace metals found in petroleum.

Table 1.2 Relative stability of the metalloporphyrins.

Table 1.3 Metal enrichment factors on marine organisms.

Table 1.4 Time schedule for the Delayed coke process.

Table 1.5 Typical specifications for calcined petroleum cokes.

Table 1.6 Effect of impurities on the air oxidation of graphite.

Table 1.7 Effect of temperature and water vapour partial pressure on the equilibrium partial pressure of HCl produced by the high temperature hydrolysis of NaCl and CaCl_2 .

Chapter 2.

Table 2.1 Experimental conditions for the atomic absorption spectrophotometer.

Chapter 3.

Table 3.1 Elemental composition of Flexicoke and Delayed coke.

Table 3.2 Some physical properties of Flexicoke and Delayed coke.

Chapter 4.

Table 4.1 Vanadium and nickel extractions obtained from the aqueous leaching of as-received Flexicoke.

Table 4.2 Vanadium extraction and coke dissolution by organic solvents from as-received Flexicoke.

Table 4.3 Vanadium extraction and coke dissolution by organic solvents from Delayed coke.

Table 4.4 Infrared bands from the analysis of extracts by reaction of organic solvents with Flexicoke and Delayed coke.

Chapter 5.

Table 5.1 Key and data used in drawing the Ellingham diagrams.

Table 5.2 Variables and their maximum and minimum levels in factorial design 1.

Table 5.3 Vanadium extractions, calculated effects and analysis of variance for factorial design 1.

- Table 5.4 Nickel extractions, calculated effects and analysis of variance for factorial design 1.
- Table 5.5 Iron extractions, calculated effects and analysis of variance for factorial design 1.
- Table 5.6 X-ray diffraction data of the crystalline product from the vapour transport experiments.
- Table 5.7 Variables and their maximum and minimum levels in factorial design 2.
- Table 5.8 Confounding pattern for factorial design 2.
- Table 5.9 Vanadium extractions, calculated effects and analysis of variance for factorial design 2.
- Table 5.10 Nickel extractions, calculated effects and analysis of variance for factorial design 2.
- Table 5.11 Iron extractions, calculated effects and analysis of variance for factorial design 2 (abcd(ef) run=100%).
- Table 5.12 Iron extractions, calculated effects and analysis of variance for factorial design 2 (abcd(ef) run=100%).
- Table 5.13 Change in surface area, calculated effects and analysis of variance for factorial design 2.
- Table 5.14 Metal extractions from centre point replicate tests.
- Table 5.15 Metal concentration as a function of distance along coke bed.
- Table 5.16 Variables and their maximum and minimum levels in factorial design 3.
- Table 5.17 Vanadium extraction rates, calculated effects and analysis of variance for factorial design 3.
- Table 5.18 Nickel extraction rates, calculated effects and analysis of variance for factorial design 3.

Table 5.19 Vanadium, nickel and iron extraction from the vapour transport experiments using Delayed coke.

Appendix A.

Table A1	Effect of sulphuric acid concentration on the molar absorption coefficient of vanadium (V) solutions at various wavelengths.
Table A2	Calculated K_1 , ϵ_1^λ , and slopes and intercepts from Figure A4, for the $\text{VO}_2^+-\text{H}_2\text{SO}_4$ system.
Table A3	Calculated K_2 , ϵ_2^λ , and slopes and intercepts from Figure A5, for the $\text{VO}_2^+-\text{H}_2\text{SO}_4$ system.
Table A4	Error analysis in the calculation of β_2 in the $\text{VO}_2^+-\text{HSO}_4^-$ system.
Table A5	Effect of sulphuric acid concentration on the molar absorption coefficient of vanadium (IV) solutions at various wavelengths.
Table A6	Calculated K_1 , ϵ_1^λ , and slopes and intercepts from a $1/(\epsilon^\lambda - \epsilon_0^\lambda)$ versus $1/[\text{SO}_4^{2-}]$ plot, for the $\text{VO}^{2+}-\text{SO}_4^{2-}$ system.
Table A7	Calculated K_2 , ϵ_2^λ , and slopes and intercepts, for the $\text{VO}^{2+}-\text{SO}_4^{2-}$ system.

Appendix B.

Table B1	Some physical parameters associated with a fluidized bed of Flexicoke.
Table B2	Theoretically determined parameters for fluidized bed at various HCl flow rates.

LIST OF PLATES

Chapter 3.

- Plate 3.1 Optical microscope image of the cross-section of a Flexicoke particle, magnification= 320x.
- Plate 3.2 Optical microscope image of the cross-section of a Delayed coke particle, magnification= 320x.
- Plate 3.3 SEM of cross section of cross-section of Flexicoke particle, magnification=600x.
- Plate 3.4 Vanadium distribution of cross-section of Flexicoke particle, magnification=600x.
- Plate 3.5 Nickel distribution of cross-section of Flexicoke particle, magnification=600x.
- Plate 3.6 Sulphur distribution of cross-section of Flexicoke particle, magnification=600x.
- Plate 3.7 SEM of cross section of Flexicoke particle with pyrite particle as nucleus, magnification=600x.
- Plate 3.8 SEM of cross-section of a as-received Flexicoke particle, magnification=600x.
- Plate 3.9 Line analysis of Ni, V and S distributions in a Flexicoke particle, magnification=600x.

Chapter 5.

- Plate 5.1 SEM of cross-section of Flexicoke particle after 90 minutes of reaction; magnification=600x.
- Plate 5.2 Line analysis of Ni, V and S distributions in a Flexicoke particle after 90 minutes of reaction; magnification=600x.

INTRODUCTION.

The aim of this project was two-fold: firstly, to extract the metal values, particularly vanadium and nickel, contained in petroleum cokes; and secondly to leave said petroleum cokes in a clean form suitable for anode production. The second aim eliminated ashing techniques as a means to extract the metals since these would destroy the coke.

The extraction of vanadium and nickel from Flexicoke and Delayed coke was initially investigated by a hydrometallurgical technique. Leaching of as-received Flexicoke was not very successful in extracting the metal values from the coke. Fine grinding was required to obtain high vanadium extractions; however, grinding of the cokes was found to be difficult because of its very high work index and its tendency to agglomerate. Nickel proved inaccessible to acid leaching and less than 17% was extracted under all studied conditions. An extraction process based on leaching would required high energy costs and good control to achieve the required fine grinding for good metal extraction. Vanadium and nickel extractions from Delayed coke were poor, with only trace amounts extracted into solution.

The hydrometallurgical route was abandoned in favour of a vapour transport process in which vanadium, nickel and iron were extracted in the form of volatile metal chlorides which are transported out of the reaction zone by a flowing gas stream and which condense in cooler parts of the furnace. The process was investigated using fixed bed and fluidized bed reactors; most work was performed with Flexicoke. High vanadium and nickel extractions could be obtained from Flexicoke without the need for grinding. The preferred form of the process is that with a fluidized bed reactor because of the advantages it offers for continuous operation, excellent temperature control, good mixing, high mass transport and good compatibility with

existing Flexicoking technology. The kinetics of vanadium and nickel extraction from Flexicoke were also investigated.

The thesis has been divided into six chapters and four appendices. Chapter 1 gives a review of the previous literature relevant to the project; for completeness, a brief overview of the occurrence, origin and concentrations of metal in petroleum is also given. Chapter 2 shows the experimental procedures and materials employed during this project. Chapters 3, 4 and 5 give the results and discussion for the chemical and physical properties of the cokes, hydrometallurgical experiments and vapour transport experiments, respectively. Further results and discussions are given in Appendix A for a spectrophotometric study of vanadium (V) and vanadium (IV) complexes in sulphuric acid; the results in Appendix A are used in the discussion in Chapter 4. The data collected during the project is given in Appendix D.

1. LITERATURE SURVEY

1.1 METALS IN PETROLEUM.

1.1.1 INTRODUCTION.

The purpose of the following section is to give a brief overview of the occurrence, concentration and biogenesis of metals, particularly vanadium and nickel, in petroleum. It is not intended to be a comprehensive literature review. The presence and role of trace metals in petroleum has been extensively reviewed by Yen [1], Sugihara [2], Valkovic [31] and Jones [32].

Petroleum falls into the class of fuel which is not "clean". Beside hydrocarbons, petroleum contains the following contaminants:

- a) Non-hydrocarbons which are heterocyclics, containing sulphur, nitrogen and oxygen.
- b) Metals and minerals such as silica, salt and pyrite.
- c) High molecular weight, large asphaltic molecules.

The concentration of these contaminants may be small, but their effect is large. They are the source of environmental pollution, equipment corrosion and poisoning of process catalysts.

1.1.2. OCCURRENCE AND CONCENTRATION OF METALS IN PETROLEUM.

All petroleums contain some metal constituents. In a spectrographic determination of 23 American crude oils, Yen [1] revealed the presence of 28 metallic elements. A number of studies of crude oils from different parts of the world showed that all metals from lithium to molybdenum, with the exception of rubidium and niobium, can be present in petroleum. In addition, silver, cadmium, tin, barium, uranium, lanthanum,

cerium, neodymium, erbium and ytterbium have been detected [2]. The concentrations of these metals vary and may be higher than a thousand parts per million for vanadium, somewhat less for nickel, and appreciably less for other metals, running to amounts considerably less than one part per billion. The typical concentration ranges of the principal trace metals found in petroleum are given in Table 1.1 [16].

Element	Concentration range, ppm
Cu	0.2-12.0
Ca	1.0-2.5
Mg	1.0-2.5
Ba	0.001-0.1
Sr	0.001-0.1
Zn	0.5-1.0
Hg	0.03-0.1
Ce	0.001-0.6
B	0.001-0.1
Al	0.5-1.0
Ga	0.001-0.1
Ti	0.001-0.4
Zr	0.001-0.4
Si	0.1-5.0
Sn	0.1-0.3
Pb	0.001-0.2
V	5.0-1500
Fe	0.04-120
Co	0.001-12
Ni	3.0-120

Table 1.1 Typical concentration ranges of the principal trace metals found in petroleum.

Whoodle and Chandler [3] and Scott et al [13] found a linear relationship between the vanadium content of crudes and their viscosities; the heavier the crude the greater the vanadium content. The correspondence of high metal content with the heavier petroleum fractions was observed by Garner et al [14], who found that 97% of the vanadium and 99% of the nickel were precipitated with the asphaltenes. Skinner [5] also found, from solvent extraction studies, that the concentration of vanadium increased as the molecular weight of the asphaltenes increased.

The vanadium to nickel ratio has been found to increase with the asphaltic content of the crude; nickel is contained in all crudes, but vanadium was particularly associated with those rich in asphalt [2]. Oils recovered from reservoir rocks of the same geological age have essentially the same vanadium to nickel ratio [3,15]. Relative increases of vanadium content, as compared to nickel, with age of the oil has been observed [15]; but the opposite trend was found with five Romanian crudes, in which enrichment of nickel occurred with age [2].

The metal components in petroleum can be classified into the following categories [1]:

- a) Metalloporphyrin chelates.
 - (aa) Vanadyl and nickel porphyrins.
 - (ab) Chlorophyll- α and other hydroporphyrins.
 - (ac) Highly aromatic porphin chelates.
 - (ad) Porphin decomposition ligands.
- b) Transition metal complexes of tetradentate mixed ligands, such as those formed with vanadium, nickel, iron, copper, cobalt and chromium.
 - (ba) Simpler complexes from resin¹ molecules.
 - (bb) Chelates from asphaltic² sheets.

¹ Resins are a chemically indeterminate mixture of compounds precipitated from bitumen, petroleum residua, or coals with non-polar hydrocarbon solvents. They are the fraction soluble in n-pentane but insoluble in n-propane

² Asphaltenes have been defined by solubility behaviour similar to resins. They are the fraction soluble in n-heptane but insoluble in n-pentane.

- c) Organometallic compounds such as those of mercury, antimony and arsenic.
- d) Carboxylic acid salts of the polar functional groups of resins, such as those of molybdenum and germanium.
- e) Colloidal minerals such as silica, pyrite and NaCl.

In the above list there are only two important classes of metals: the porphyrin metals (class aa) and the non-porphyrin metals (classes ab, ac, ad, ba and bb). The former class has been extensively studied [1, 2, 4-7], while the latter has received little attention.

1.1.2. a) Metalloporphyrins.

Porphyrins are pigment compounds composed basically of four pyrrole units linked together with methine bridges. They are essentially planar molecules with highly conjugated bonding, giving rise to a high degree of aromatization.

The presence of metalloporphyrins in bitumens, coals and shales was discovered in 1934 by Theibs [8]. In these porphyrins he identified the presence of vanadium as well as iron. Since then numerous investigations [1, 2, 5-7] have confirmed the presence of vanadium porphyrins in a large number of crude oils, as well as in oil sands, sedimentary rocks, precambrian rocks and coal [4, 33]. More recently nickel porphyrins have been identified and isolated [1].

Metalloporphyrins account for only a small proportion of the metal content in petroleum. The majority of metal porphyrins found in petroleum are vanadyl and nickel porphyrins. Possibly other cations, such as iron [8], copper and zinc, are involved; but if they do exist, they do so in very low concentrations [4].

A large number of investigations has been reported on the isolation and identification of the porphyrins. Figure 1.1 gives a few of the variations found.

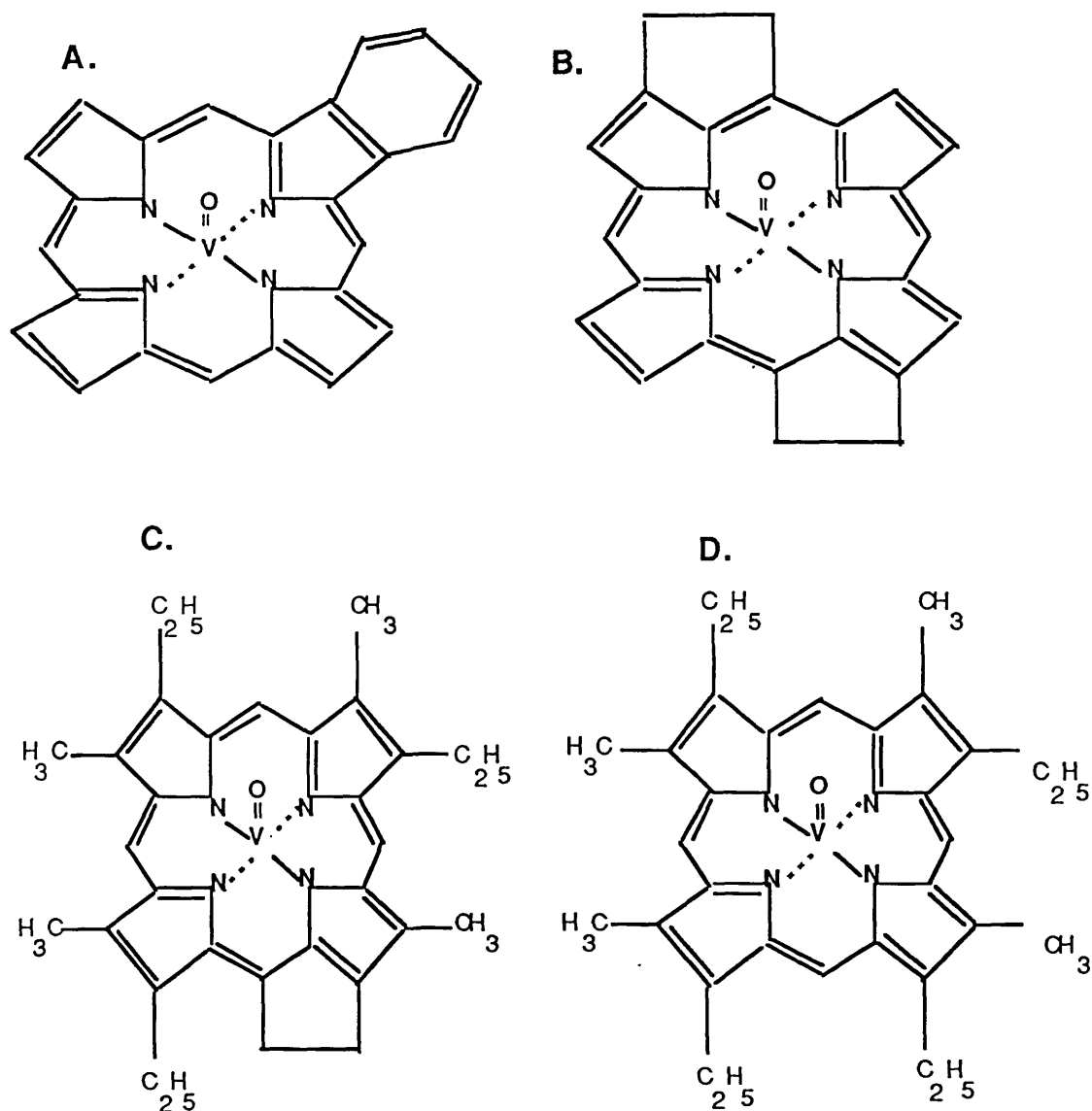


Figure 1.1 Various vanadyl porphyrin structures [1]. (A) Vanadyl benzoporphyrin; (B) Vanadyl porphyrin structure with two cycloalkano rings. (C) The deoxophyllerythroetioporphyrin (DPEP) and (D) etio type porphyrins. The alkyl groups may vary.

1.1.2. b) Non-porphyrin metals.

The bulk of the trace metals in petroleum appears to be accommodated in this class. It includes the altered or modified porphyrin structures, such as hydroporphyrins (class ab), arylporphyrins (class ac), porphin degraded products, and

tetradentate complexes of mixed ligands. The inclusion of the altered or modified porphyrin structures into this class is reasonable as in many cases they lose the porphyrin properties, even when they exist in the same environment. For example, VO^{2+} rather than nickel can be most readily complexed with altered or modified porphyrins, unlike the corresponding reaction for porphyrins [1, 4].

Both resin and asphaltene fractions are minor components of the total crude, yet they contain a large proportion (10-50%) of the nitrogen and sulphur content of the crude. The probability of more than one resin molecule forming a metal complex is, thus, quite high. The tetradentate ligands can be a combination of any four donor atoms from nitrogen, sulphur and oxygen. They can be small, as in the ligands formed from polar resin molecules, Figure 1.2, or large as formed by asphaltic sheets. Evidence for the presence of these tetradentate complexes is as follows [1, 2, 4, 10]:

a) Two nitrogen-two oxygen, three oxygen-one sulphur, four sulphur, three sulphur-one nitrogen and two sulphur-two nitrogen tetradentate complexes have been identified.

b) Certain fractions of Boscan (Venezuelan) vanadyl porphyrins only give even masses by mass spectrometry. The only possibility is that these fractions contain odd numbers of nitrogen in the donor system.

c) Asphaltenes can have a fixed capacity for complexing metals [1, 9]. These complexing sites may be defect centres formed by the aromatization of hydrocarbon skeletons containing sulphur, nitrogen and/or oxygen.

During the formation of asphaltenes the graphitization process is interrupted by the divalent nature of sulphur and oxygen and the trivalent nature of nitrogen. As a result "gaps" or "holes" are formed in the fused benzene network; these "holes" are sites of donor atoms, and metals will be able to complex into these sites. The "holes" are much more stable complexing sites than the tetradentate resin complexes.

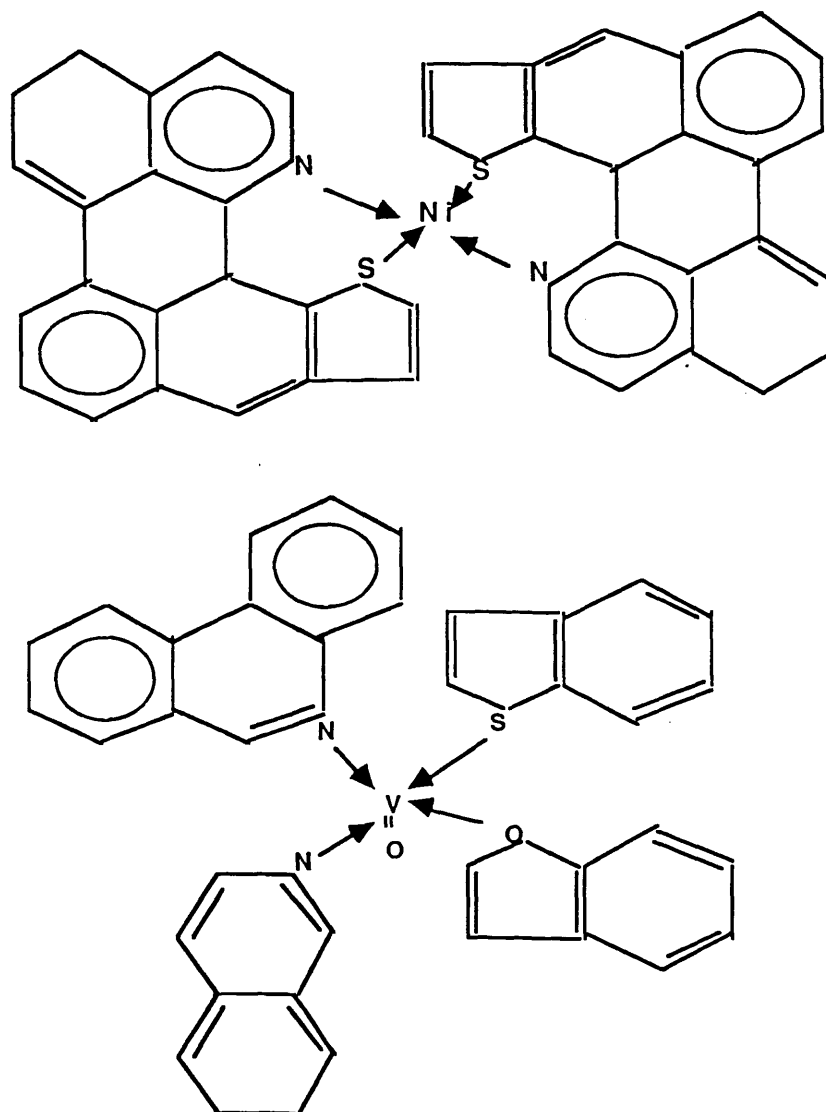


Figure 1.2 Example of the complexes of tetradentate ligands [1].

1.1.3. ORIGIN OF METALS IN PETROLEUM.

The metals contained in the organic matrix of crude oils may have originated in several ways [10]:

- a) Through incorporation and diagenesis of metal complexes in the original biological material.
- b) Through incorporation into the organic matrix during

diagenesis of the biological material in source rocks either from clay minerals or interstitial aqueous solutions.

c) Through uptake from an aqueous phase or mineral.

Most authors agree that the metals in petroleum were derived from primary biological material. Hodgson [11] in his study of vanadium, nickel and iron in Canadian crudes deduced that the metals entered the oil early in its history, and that the original organic matter was the source of the metals. Yen [1] and Skinner [5] reported similar findings for American crudes, and indicated that loss or gain of metals during migration was unlikely. Hyden [12], however, concluded that only the concentration of nickel and vanadium reflected the composition of the organic material, and that other elements, such as copper and uranium, were introduced from the source rock, the reservoir rock or during migration. Gulyaevov and Punanova [1] who studied the distribution of 25 elements in Russian petroleums concluded that all metal concentrations, except that of vanadium, could be accounted for by their concentrations in the original biological materials. The excess of vanadium was attributed as originating from source rocks. A similar argument has been proposed to account for the very high vanadium content (1000-1200 ppm) in Venezuelan Boscan crude, although this is known to contain an unusually high content (40%) of vanadyl and nickel porphyrins [2].

It is generally agreed that petroleum arises from biological substances, and that porphyrin compounds originate from chlorophyll- α and/or hemoglobin [1, 5]. The removal of magnesium from the chlorophyll- α structure is governed by chemical stability, and as shown in Table 1.2 below, its removal is relatively easy; whereas removal of the vanadyl ion is difficult. It is reasonable to expect that the removal of Mg can be accomplished under natural conditions and that it occurred soon after decaying, and possibly before burying [1].

Metal Cation	Removed by
Ag(I), K(I), Na(I), Pb(II), Hg(II)	Water
Zn(II), Cd(II), Fe(II), Mg(II)	Dilute HCl
Cu(II), Mn(II), Co(II), Ni(II), Fe(III)	Concentrated H ₂ SO ₄
VO(IV)	HBr-Acetic acid
VO(IV) ³	Trichloroacetic acid

Table 1.2. Relative stability of the metalloporphyrins.

In support of the above argument chlorophyll- α is only observed in limited cases, yet pheophytin- α as well as other intermediates, such as pheoporphyrin and phylloerythrin have been identified in recent sediments [1, 6]. The sequence shown in Figure 1.3 represents a proposed transformation from chlorophyll- α to deoxophyllerthroetioporphyrin (DPEP) [1]. The drive for this change is an increase in chemical stability; the activation barrier is overcome by heat and pressure arising from burial depth. Indeed, the compounds present in the lower part of the sequence shown in Figure 1.3, are found in deeper, older sediments, while the inverse is true for those compounds in earlier part of the sequence [1].

Further evidence for the biological origin of porphyrins lies in the fact that synthetic porphyrins prepared from chlorophyll- α and from hemoglobin have spectra similar to those porphyrins found in petroleum. The presence of hemoglobin-type compounds is not positive proof that animal decomposition products were involved in the formation of petroleum as some root nodules may contain hemoglobin [6].

³ Porphyrin ligand complexing to the VO²⁺ cation is tetra-m-s-4-biphenylporphin.

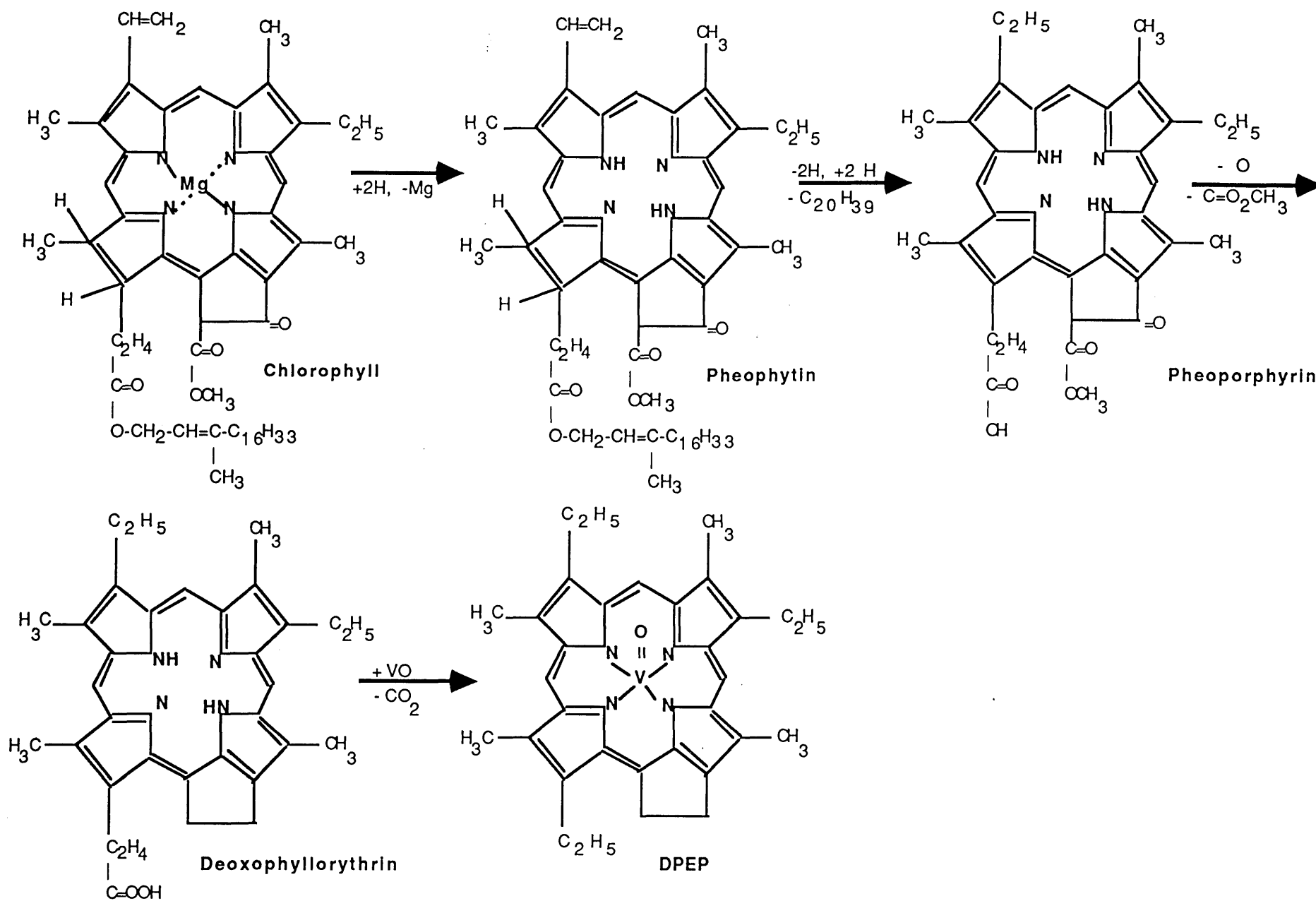


Figure 1.3 Hypothetical scheme from Chlorophyll to DPEP [1].

The presence of vanadium and nickel in petroleum can be explained by their concentration in some marine organisms [1, 4-6, 11]. It has been found that the metals concentrated by fresh water shales are different from those of marine shales. For example, in marine shale the most concentrated metals are vanadium and nickel, whereas in fresh water shales the metals are copper, lead, zinc and tin. Certain metals are enriched in brown algae and marine animals from 10 to 280,000 times, as compared to sea water, as shown in Table 1.3 below.

Element	Brown algae (Fresh weight)	Marine Animals. (Dry weight)
Ni	200-1800	5000-41000
V	10-5000	17000->280000
Zn	400-1400	32500
Co	4500-13000	7000-21000
Mn	17000	-
Fe	10700	-
Cu	330-880	-

Table 1.3. Metal enrichment factors of some marine organisms.

The vanadium content in various forms of ascidia (sea squirts) was found to be as high as 6520 ppm on a dry basis. In ascidians and holothurians, vanadium pigments are found in blood cells, i.e. in *Phleusia manillata* and *Ascidia mentula* 80% and 10%, respectively, of the total vanadium is in the blood [1]. Clams, scallops and oysters are rich in nickel; for example, *Cordium edule* (common edible cockle) contains 20 ppm on a dry basis.

The introduction of nickel into the porphyrin structure should be easier (under less drastic conditions) than that of vanadium, due to their relative stabilities. Indeed, more recent petroleum sediments are richer in nickel than older sediments. These observations have led to a number of studies relating the vanadium to nickel ratio to the age of the crude, but no definite correlation has been found [1,2].

1.1.4. CONSEQUENCES OF THE PRESENCE OF METALS IN PETROLEUM.

Until quite recently the demetallisation of petroleum was of very little importance [17]. It was not until the industrialized and some developing nations introduced pollution control legislation that these minor constituents of petroleum received some attention. The major source of pollution from petroleum refineries is sulphur dioxide emissions, and it has been found that the catalysts employed for desulphurization are poisoned by the metals in petroleum. Furthermore, decreasing petroleum reserves have forced refiners to use heavier crudes, such as those from the Athabasca tar sands and Orinoco tar basin, which tend to contain high amounts of sulphur. Thus, it became necessary to either demetallise the petroleum before desulphurization or to introduce completely new processes for upgrading the crude oils which were not affected by the presence of metals.

The removal of metals from petroleum is a complex problem for the following reasons [1]:

- a) Metals are chelated or complexed to ligands that are completely compatible with petroleum and make separation difficult.
- b) The metal concentration is very low, usually ranging from 1 to 10,000 ppm; vanadium is the most abundant metal.
- c) Metals are usually associated with contaminants such as heterocyclics and the asphaltic fraction.

d) Metals can exhibit catalytic effects during conversion. Demetallisation may cause odd effects.

e) Refining and upgrading often involve the use of catalysts, which may be poisoned by metals.

Metals in petroleum are, thus, very important in the sense that they hold the key to profitable petroleum refining.

1.2. UPGRADING PROCESSES USED FOR HIGH METAL CONTENT PETROLEUM.

1.2.1 INTRODUCTION.

The extensive use of catalysts in the oil industry for improving gasoline yield and quality and to desulphurize petroleum has lead to considerable interest in trace metals in petroleum. Although in desulphurization and hydrogenation the major problem is high nitrogen levels in crude oils, the presence of metals, particularly vanadium, complicate the operations by complexing with nitrogen containing compounds (and, thus, reducing the efficiency of the nitrogen removing steps) and by poisoning and blocking the catalyst in their own right. One of the most successful modern desulphurization techniques, the Gulf Oil Hydrodesulphurization (HDS) process, was found to be economic only when processing light petroleums with less than 150 ppm total metal content [17].

Processes such as the various forms of catalytic cracking proved initially unsuccessful in dealing with highly viscous, high metal content crude oils. The catalytic cracking processes consist of cracking the petroleum at a given temperature and pressure (which depend on the feedstock), in the presence of a catalyst. The various processes currently employed in catalytic cracking differ mainly on the method of catalyst handling [16]. Metal accumulation, and simultaneous poisoning of catalysts can be eliminated or controlled by [16]:

- a) Feedstock selection.
- b) Increasing catalyst addition rates.
- c) Removal of metals from feedstocks.
- d) Treatment of catalysts after accumulating the metals.

In order to cope with high metal content petroleum, processes were developed to regenerate the catalyst by removing the deposited metals. Two such processes are the Demet and the Met-X processes.

The Demet process [16] consists of two pretreatment steps followed by a washing stage. In the first stage the catalyst is treated with a sulphurous compound to remove vanadium, followed by reaction with an anhydrous chlorinating agent (such as dry chlorine) to remove nickel and then washing with an aqueous solution of a chelating agent (such as citric acid). The catalyst is dried and retreated before returning to the cracking unit.

In the Met-X process [16] the contaminated catalyst is cooled and mixed in a stirred reactor with an ion exchange resin slurry which contains sulphuric acid. The resin loaded with the metals is separated from the catalyst in an elutriator, and regenerated by washing with aqueous sulphuric acid. The clean catalyst is filtered, slurried with oil and pumped into the catalytic cracker feed system.

The use of the above regenerating processes has to be balanced against product value and operating cost. Often the most economic route for upgrading high metal petroleums involves coking processes. The new emphasis on the use of heavy crude oils either through secondary recovery, or from tar and oil sand formations has caused renewed interest in coking processes. Three coking processes have been commercially proven: Delayed coking, Fluid coking and Flexicoking.

1.2.2. COKING PROCESSES.

As the samples available for experimental work are those produced by Delayed coking and Flexicoking, only these two processes will be described in detail.

1.2.2. a) Delayed coking process.

Delayed coking was first introduced as a commercial process in the 1930's [18]. It was developed to process fresh or cracked petroleum residua into lighter products such as naphtha, fuel oil, gas oil and a residual coke. The coke is generally high in sulphur and metals. The process has remained essentially the same as that introduced 50 years ago, but a number of technical innovations have allowed it to continue to attract interest.

Delayed coking is a semi-continuous process in which the heated feed liquids are transferred to large drums where coke deposition takes place. In early refineries severe thermal cracking of the residual fuel oils resulted in the unwanted deposition of coke in the heaters. With improved design it was found that the feed temperature could be raised above the coking temperature without significant coke formation. To achieve this, high pumping velocities through the heater were required, and an insulated drum was provided on the effluent side of the heater, thus allowing the long residence time needed for the cracking reactions to proceed to completion [16, 18-22].

Figure 1.4 shows schematic diagram of the Delayed coking process. Hot fresh liquid from the vacuum distillation tower is fed into the fractionator, two to four trays above the bottom vapour zone. Introducing the feed at this level accomplishes the following [19]:

a) The hot vapours returning from the coke drums are quenched by the cooler feed liquid preventing any significant amount of coke formation and simultaneously condensing a

portion of the heavy hydrocarbons which are recycled to the coke drums.

b) Any material with a boiling point lower than the desired coke drum feed is vaporized from the fresh feed liquids.

c) The fresh liquid feed is further preheated.

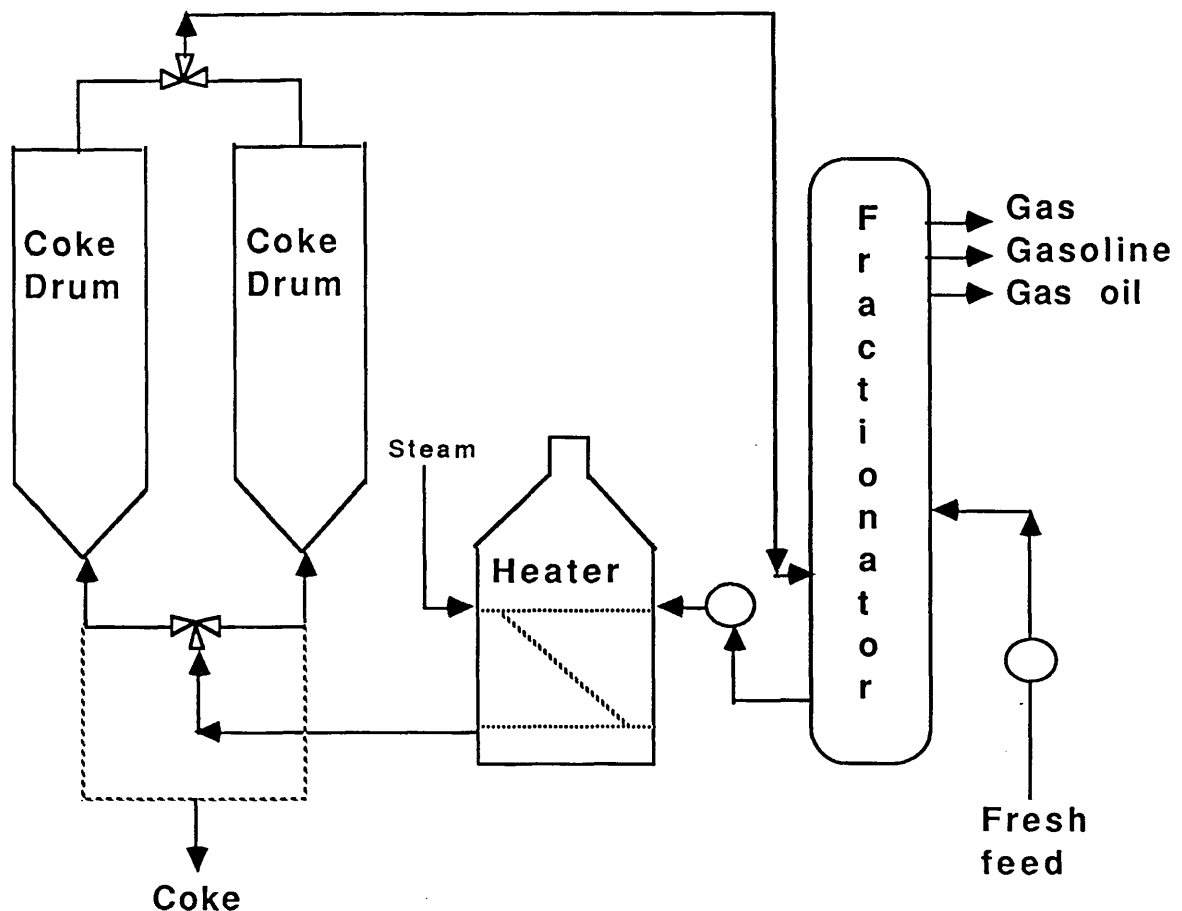


Figure 1.4 Delayed coking process flow diagram.

The feed liquid, combined with the overhead vapours, is pumped through the coker furnace, where it is heated from about 270°C to about 480°-515°C. The feedstock temperature is carefully monitored to control the final volatile level of the coke. A multiple steam injection system is used to adjust residence time and liquid feed velocity in the furnace tubes [18].

The heated feed liquid then passes through a three-way switch valve where it is directed to the bottom of one of the coke

drums. Cracked vapours leave the top of the filled drum and are quenched in the fractionator by the incoming feed liquid. The temperature of the coke drum ranges from 415° to 450°C, at pressures ranging from 15 to 90 p.s.i. [16].

When the coke drum in use is filled to a safe margin from the top, the heater effluent is switched to the other drum. The full drum is isolated, steamed to remove any remaining hydrocarbon vapours, cooled by filling with water, opened, drained and the coke removed. The removal of the coke is carried out either mechanically or hydraulically [18, 19, 21]. A typical time schedule for the operation is given in Table 1.4 [19].

Operation	Time (hours)
Fill drum with coke	24
Switch drum and steam out	3
Cool drum	3
Drain cooling water	2
Open drum and decoke	5
Close drum and test	2
Heat up	7
Spare time	2
	Total: 48

Table 1.4 Time schedule for the Delayed coke process.

Although the exact mechanism involved in the formation of Delayed coke is not known three distinct phenomena can be noted [18]:

- a) Partial vaporization of low boiling hydrocarbons and mild cracking of the feed as it passes through the furnace.
- b) Cracking of the vapour as it passes through the drum.
- c) Successive cracking and polymerization of the heavy

liquids trapped in the coke until they are converted to low boiling hydrocarbon vapours and coke.

Two processes similar to Delayed coking are in commercial operation. The Decarbonizing process is designed to reduce coke and gasoline yields, but to produce maximum yields of gas oil. The main difference with Delayed coking is that lower pressures and temperatures are used (415° and 485°C in the coke drum and heater, respectively; and 10 to 25 p.s.i.). The Low-Pressure coking process is also similar to the Delayed coking process. The operating conditions are 435°C and 25 p.s.i. Excessive coke formation is prevented by addition of water to the feedstock [16]

1.2.2. b) Flexicoking process.

The Flexicoking process was developed by Exxon Research and Engineering, and first put into commercial operation in 1976 at Toa Oil Co. Ltd., Kawasaki, Japan. It is a process designed to treat high boiling petroleum fractions, such as vacuum distillation tower residua, into valuable liquid hydrocarbons, low sulphur fuel gas and a residual coke. The coke produced in the Flexicoking process is quite different to that produced by Delayed coking [23]. In Delayed coking the quality of the coke is wholly dependent on the quality of the liquid feed, and essentially all the sulphur and the metals end up in the coke. In Flexicoking the gasification of the coke produces a substantial concentration of the metals in the coke and at the same time significant desulphurization is obtained [23-25].

Flexicoking is a continuous coking-gasification process carried out in three vessels, as shown in Figure 1.5. The vessels, containing fluidized coke, are interconnected to permit transfer of solids from one vessel to the other. The process typically converts 98 wt% of a vacuum residuum to gaseous and liquid products. More than 99% of the metals in the feed are concentrated in a 2 wt% solid purge from the system.

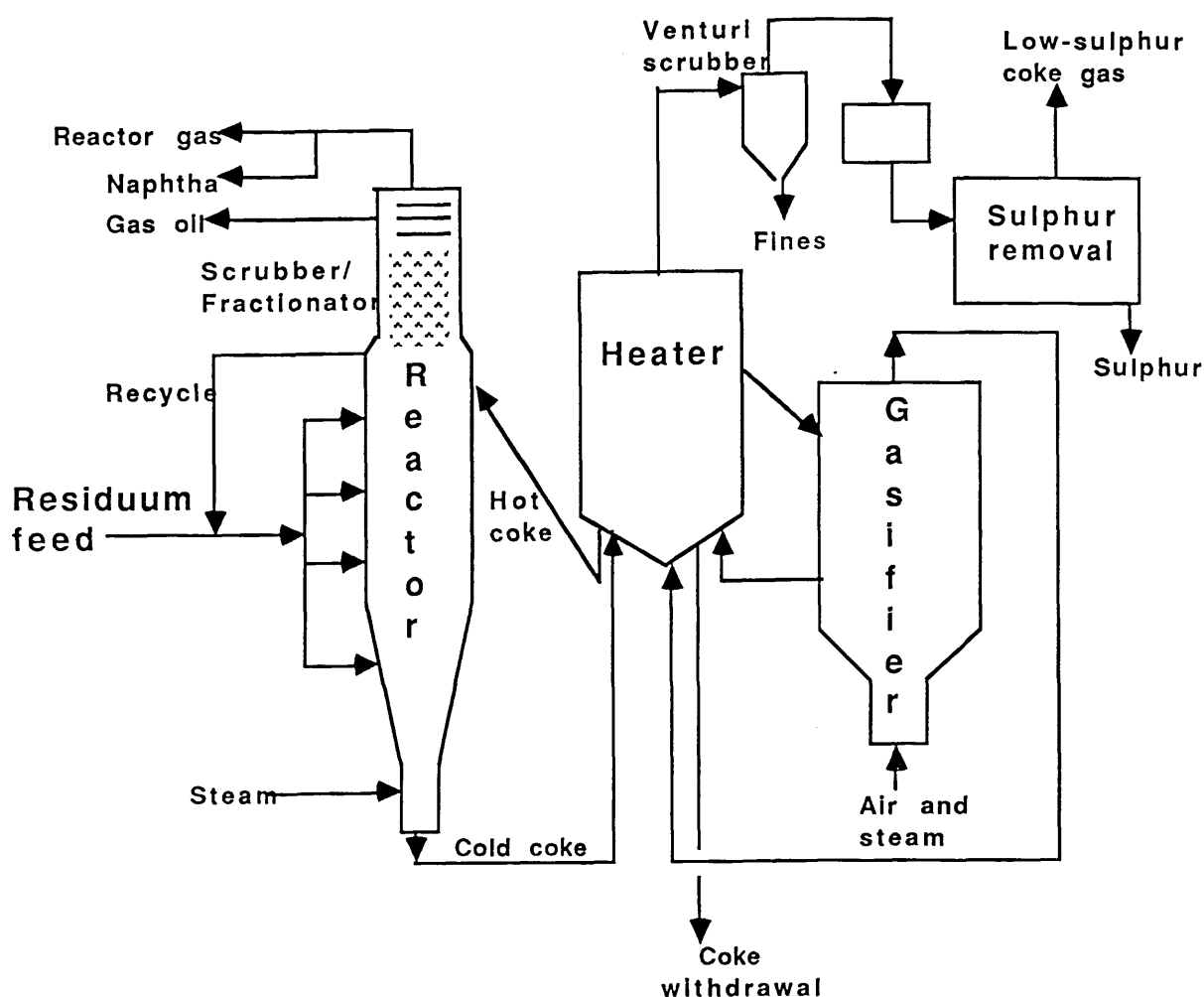
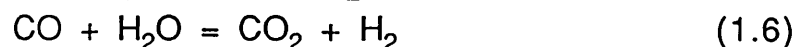


Figure 1.5 Flexicoking process flow diagram.

Residuum feed is injected into the coker reactor at a temperature of 270° to 380°C, where it is thermally cracked, typically at 510° to 535°C, to a full range of vapour products and a coke product which is deposited on fluidized coke particles. The sensible heat, heat of vaporization and endothermic heat of cracking of the residuum is provided by a circulating stream of hot coke from the heater [26]. Cracked vapours produced are quenched in the scrubber vessel, where the higher boiling fractions are condensed and if desired may be recycled back to the coking reactor. The lower boiling fractions proceed overhead from the scrubber into a conventional fractionator, where they are split into the desired liquid products [25-27].

Reactor coke product, withdrawn from the reactor with circulating coke, flows to the heater where it is heated by coke and gas from the gasifier, and partially devolatilized, yielding a small amount of light hydrocarbon gas and residual coke. A circulating coke stream is sent from the heater to the gasifier where it reacts at an elevated temperature (810° to 980°C) with air and steam to form a mixture of H₂, CO, N₂, CO₂, H₂S and a small quantity of COS [25-28]. The gasifier product gas, known as coke gas, plus entrained coke particles are returned to the heater where they are cooled to about 620° to 670°C to provide a portion of the heat which is carried to the reactor [24, 27].

In the gasifier the following reactions take place:



Under the operating conditions of the gasifier, reactions 1.1 to 1.3 and 1.6 are very fast. Reactions 1.4 and 1.5 are the rate determining reactions. Oxygen entering the bottom of the coke bed can react in two ways. If it reaches a coke particle it reacts to produce a mixture of CO and CO₂ (reactions 1.1 and 1.2). Secondly, oxygen can react in the void space between particles with the CO already formed, to produce more CO₂ (reaction 1.3). Through most of the bed the slow Boudouard reaction (reaction 1.4) and the steam gasification reaction (reaction 1.5) dominate. Composition of the gasifier overhead gas, which is sent to the heater, is finally set by the water-gas shift reaction (reaction 1.6) at the gasifier bed temperature [27].

The sulphur in the residuum feed ends up in all the product fractions, with about 34% of it being concentrated in the reactor coke. Some 97% of this sulphur is then gasified with the coke to form H_2S , which can be removed by any commercially available process, and some COS, which is converted to H_2S and CO_2 by low temperature hydrolysis over a fixed bed catalyst. Nitrogen compounds are also largely broken during gasification to give elemental nitrogen [26, 27].

The mechanism for the formation of Flexicoke particles [23] is the repeated deposition of a thin film of fresh coke on seed coke particles as they pass to and from the reactor and gasifier. Fines recovered from the coke gas by a Venturi scrubber are returned to the reactor to act as seed particles. Seed coke is circulated through the reactor/heater system where a layer of coke, with a typical thickness of 5 μm , deposits. The reactor/heater coke is transferred to the gasifier where a portion of the freshly deposited coke is gasified, and the remaining coke is returned to the reactor/heater where additional coke deposits

The Flexicoking process produces a substantial amount of low-heating value coke gas, which due to its high nitrogen content, makes the recovery of hydrogen and/or synthesis gas economically unattractive. In order to overcome this problem a Dual-Gasification Flexicoking process was introduced in 1981. In this system the reactor and heater function in exactly the same way as in conventional Flexicoking, but two gasifiers are employed: one is an air gasifier and the other a steam gasifier. The coke produced is in no way different from conventional Flexicoke [28-30]. No commercial units of the Dual-Gasification Flexicoking process are presently in operation.

Fluid coking was the predecessor to Flexicoking; essentially it is the same process, but only the reactor and heater are employed. No gasification of the coke takes place, with the result that more coke is produced (typically 9 to 10 wt% of the residuum feed), with higher sulphur and lower metal content.

1.3 PETROLEUM COKES AND ITS USES

1.3.1. PETROLEUM COKES.

Jack et al [73] have examined samples of Delayed coke, Fluid coke and Flexicoke produced from Athabasca oil sand bitumens. They observed that the particle size distribution for Flexicoke indicates two types of particles in the size ranges 0.10-0.15 mm and 1-10 mm in diameter. The larger particles result from the agglomeration of smaller particles into very porous spherical aggregates. The smaller Flexicoke particles are roughly spherical and are reported to be quite porous. The internal structure of the fracture particle shows an "onion skin" appearance expected from the repeated deposition of thin layers of coke on the seed particles. Delayed coke by contrast showed a wide particle size distribution and irregular particle shape, expected from the hydraulic or mechanical removal of the coke from the coking drums. No macroporosity was evident in these particles and their surface was smooth.

Mettrailer et al [23] reported the specific surface area of Flexicoke produced under 60% gasification conditions to be about 100 m²/g; and the density of the coke particles from various bitumens to vary from 1440 to 1920 Kg/m³. Matula et al [25] found a slightly lower coke particle density (for a coke produced at gasification levels greater than 95%) of 1360 to 1440 Kg/m³. They also reported a coke bulk density of 800 to 870 Kg/m³.

In another work, Jack et al [63], found the concentration of vanadium in as-received Flexicoke was dependent on particle size. For a coke with bulk concentration of 8010 ppm, they found that fine particles (0.125-0.150 mm) contained 7570 ppm, medium sized particles (0.150-0.212 mm) contained 9800 ppm and large particles (2.8-5.7 mm) contained 9185 ppm vanadium. No such particle size dependence is reported for other metals or for sulphur. The authors also found that Fluid coke particles are

non-porous and have a vanadium-rich core in the centre of the particle surrounded by a surface zone quite low in vanadium. A similar distribution for sulphur was found by Mettrailer et al [23] in Flexicoke.

Jack et al also found that Delayed coke particles were hydrophobic giving a contact angle of 57 degrees with 1M H₂SO₄. A benzene-extractable material unique to Delayed coke was obtained; elemental analysis revealed this material to consist of 78.51% C, 5.38% H, 0.95% N and 6.60% S, with no v-S-H or v-N-H stretching frequencies evident in the infrared spectrum. They speculated that the presence of this material rendered the coke hydrophobic; however, after benzene-extraction the wettability of the coke decreased, giving a contact angle of 95 degrees with 1M H₂SO₄. The use of (unspecified) surfactants made the coke surface hydrophilic, with a contact angle of zero degrees. Flexicoke particles were found to show excellent wettability in aqueous solutions.

Both Flexicoke and Delayed coke are reported to contain a greater amount of vanadium than nickel; however, the vanadium to nickel ratio are similar in all cases [63, 73]. Flexicoke contains between five and eighty times more metal than Delayed coke, depending on the level of gasification and the petroleum feed used. The heteroatoms to metal ratio is considerably smaller in Flexicoke than in Delayed coke.

The chemical state of the metals in the petroleum cokes is not known. Jack et al [41] report that a portion of the nickel present in Flexicoke can be easily extracted by water leaching, and that sulphate was found in the leachate as the counter ion in a molar ratio of 1:1 with nickel. Thus, they inferred that a portion of the nickel exists in a simple ionic form, such as nickel sulphate. They assumed iron to be present as iron sulphide, and vanadium to exist in the +4 oxidation state (from their observations that vanadium was realized as the oxovanadium (IV) ion in non-oxidative acid leaching of Flexicoke). Vessely [68] assumed vanadium to be present in

Delayed coke as V_2S_3 , and nickel as NiS . Schemel et al [74] assumed vanadium to be present in Venezuelan Flexicoke as V_2O_3 . Most authors working with fly ash have assumed the presence of V_2O_5 , but V_2O_3 and V_2O_4 may be intermediate steps to the conversion of organo-vanadium compounds to vanadium pentoxide [75]. Indeed, Allen et al [76] have found that V_2O_5 is not formed until the final stages of combustion, i.e. when all the carbon has been burned.

1.3.2. METAL EXTRACTION FROM PETROLEUM RESIDUES.

Two types of residue materials have been considered for metal extraction: petroleum cokes and fly ashes. The latter results from the combustion of the cokes, tars and pitches. The recovery of vanadium from fly ashes has been carried out for many years. Power stations burning petroleum, and particularly Venezuelan and Californian crude oils, have sold their ashes to ferrovanadium producers. In 1965 the first integrated commercial operation to recover vanadium from fly ash was opened in Canada. No commercial operation for the recovery of metals from petroleum cokes has taken place.

1.3.2. a) Metal extraction from fly ashes.

The earliest successful attempt to extract vanadium from fly ash as an integrated process was in 1965 by Petrofina in Montreal, Canada [34, 35]. Until 1961 their Fluid coke was sold for fuel and for electrode manufacture, but the more attractive economics of coke-generated steam led to the installation of coke-fired steam boilers. The fly ash obtained from the boilers was the feed to the vanadium recovery plant; it contained about 15% vanadium and almost 60% unburned coke. Vanadium was recovered by leaching the fly ash with sulphuric acid in an agitated vessel for 4 hours at 50° to 90°C, and at a pH of 0.2 to 0.3. The pregnant leach liquor was then oxidized with aqueous sodium perchlorate, to ensure that all the vanadium was in the 5+ oxidation state, and hydrated vanadium pentoxide

precipitated by raising the solution pH, from 0.3-1.7 to 2.1, with ammonia additions. The V_2O_5 thus obtained was then filtered, dried, fused under an oxidizing atmosphere and cast onto a water cooled wheel where a thin ribbon of V_2O_5 was formed. Recoveries of 90%, or better were obtained [34, 35]. A flow sheet for the process is shown in Figure 1.6. A similar process is believed to have been used by the Long Island Lighting Company, USA [40]. No nickel recovery was attempted by either company. Both processes closed down in the late 1970's.

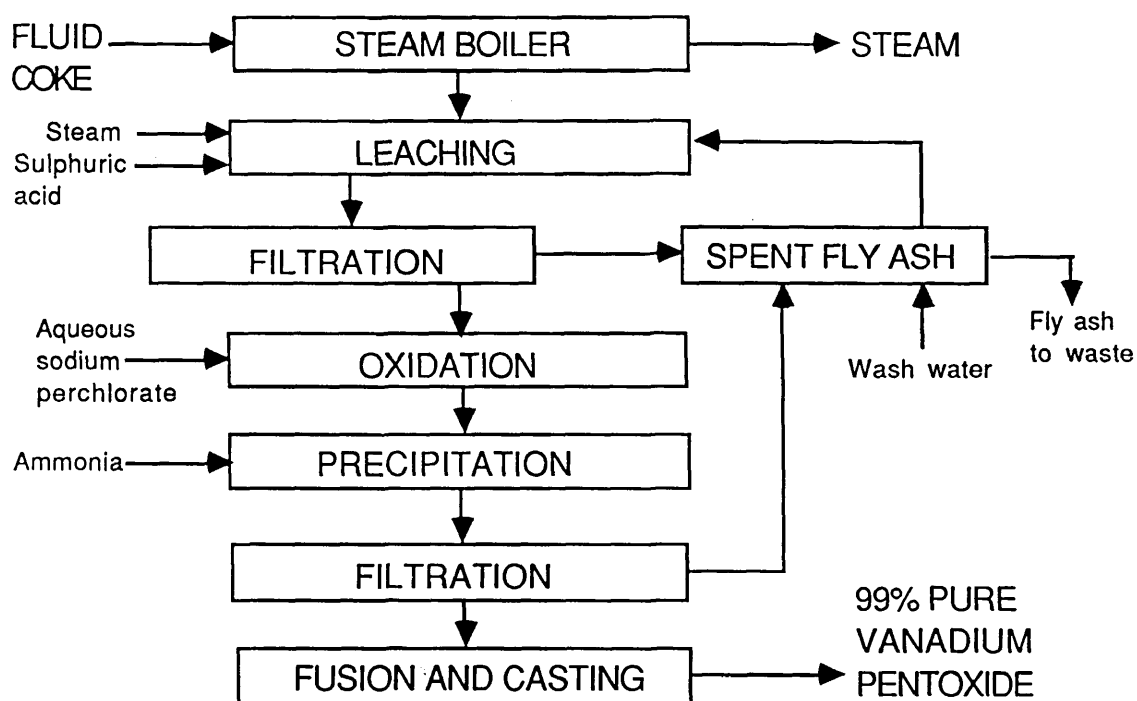


Figure 1.6 Flow diagram of Canadian Petrofina process.

Sirianni and Viens [36] and Stemerowicz et al [37] have proposed three pyrometallurgical routes for the recovery of vanadium and nickel from Canadian fly ash. The main difference between Canadian and Venezuelan fly ashes is that the former contains considerable amounts of silicates (about 25%) and aluminosilicates (about 15%), producing glassy compounds when the cokes are fired at high temperatures [36-39]. The proposed high temperature routes are:

a) Smelting the fly ash to produce a nickel matte and ferrovanadium. The process was carried out in two stages in which a nickel matte and a vanadium (and iron) bearing slag were produced. The slag was then reduced with aluminium or silicon to produce ferrovanadium. A matte containing up to 40% nickel and a low-grade iron-vanadium alloy, containing 16% vanadium, were produced. Work on the process was discontinued as no further improvement on the grade of the iron-vanadium alloy to commercial ferrovanadium grade (50-55% V) was expected. Furthermore, the process showed poor selectivity: the nickel matte containing significant amounts of vanadium (0.17-4.05%) and the ferrovanadium containing appreciable nickel (about 1.2%).

b) Smelting the fly ash to produce ferronickel and ferrovanadium. This is a two stage, selective oxidation process. In the first stage, the fly ash is smelted with a controlled amount of carbon to selectively reduce nickel and iron oxides to a nickel alloy leaving a vanadium rich slag which is reduced to ferrovanadium in the same way as in process (a). The process was discontinued because it suffered from the same lack of selectivity as process (a).

c) Smelting to produce an alloy containing most of the nickel and vanadium, and a discardable slag. Again a two stage process was envisaged, in which the molten oxides of nickel, iron, vanadium and some silicon were reduced to produce an alloy containing nickel and vanadium plus sufficient silicon to ensure adequate removal of vanadium from the slag. In the second stage of the process, the Ni-Fe-V-Si alloy would be carefully blown with oxygen to selectively oxidize the silicon and vanadium, producing a slag rich in vanadium oxides, and leaving behind a ferronickel alloy. The production of the Ni-Fe-V-Si alloy was successful, but the second stage was not attempted. This process was the best of the three, eliminating the high slag to matte ratios which caused poor selectivity in the first two processes. However, the nickel and vanadium losses were still high.

The fly ash was preroasted in all cases to remove excess carbon. All three processes are complicated, require careful monitoring and control, preroasting, high temperatures, have pollution problems and lack selectivity. Not surprisingly they were abandoned.

Schneider and George [38] obtained poor vanadium and nickel recoveries from the acid leaching of fly ash obtained from burning Canadian Delayed coke. The vanadium recovery was enhanced by roasting the fly ash at 900°C for 18 hours before leaching. No increase in extraction was observed when the roasting was carried out at 500°C. Preroasting at 500°C had no effect on the nickel extraction, but at 900°C it decreased the extraction from 20% to 2%. Poor nickel and vanadium extractions were also obtained from the leaching of Fluid coke fly ash. They also found that metal recovery was highly dependent on the coke ashing temperature, as shown in Figure 1.7. Ashing at 600°C gave almost complete vanadium and nickel recoveries, but as the temperature increased the recovery decreased. They suggest this is due to the incorporation of metal oxides, particularly nickel oxide, into a glassy silicate matrix. Using a fly ash produced from bitumen burned in their laboratory they showed that additions of Ca(OH)_2 or limestone to the bitumen, prior to coking, considerably enhanced the metal recoveries. They claim the reason for increased metal recovery to be due to either a slow down in the rate of silicate formation or preferential formation of calcium silicates.

Jack et al [41] examined the leaching behavior of Canadian Flexicoke and Delayed coke fly ash and also found the ashing temperature to be the most important factor in the successful leaching of the fly ash. Ashing at 500°C gave vanadium recoveries of 80% and 86%, and nickel recoveries of 76% and 93%, for Flexicoke and Delayed coke fly ash, respectively. However, at this ashing temperature little calorific value is obtained from the burning of the cokes. At 1000°C the metal recoveries dropped below 30% for vanadium and 20% for nickel.

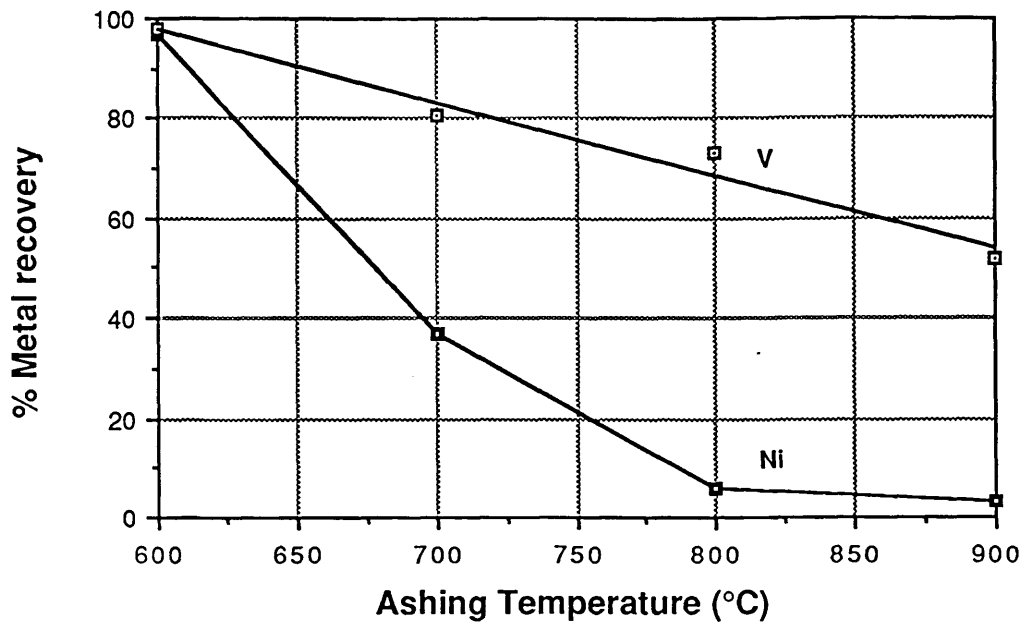


Figure 1.7 Effect of ashing temperature on the metal recovery from Canadian Delayed coke fly ash [38].

Jack et al [41] found by electron probe microanalysis of Delayed coke fly ash that the vanadium, nickel and iron appeared to be contained in an aluminosilicate matrix, which would not be susceptible to acid leaching. Griffin and Etsell [42] have, however, suggested that the vanadium may not be associated with the aluminosilicate matrix, and in a more recent publication [43] report that fly ash consists essentially of aluminosilicate spheres, and carbon granules. Cenospheres⁴ and pleuroospheres⁵ were also found in the ash. They have identified, from x-ray diffraction studies, an iron vanadium oxide, $\text{Fe(III)}_{2.6}\text{V(III)}_{5.5}\text{V(V)}_{1.6}\text{O}_{16}$, and a number of silicates such as $\text{NaAlSi}_3\text{O}_8$ and $\text{CaAl}_2\text{Si}_2\text{O}_8$. Bird and Small [75] working with fly ash carbonaceous cenospheres obtained a weak electron diffraction pattern of a vanadium rich region. Four Bragg spacings were in good agreement with published patterns for $\text{V}_3\text{O}_5(\text{OH})_4$. Allen et al [76] working with carbonaceous fly ash confirmed the presence of V_2O_5 by Auger microscopy. Their

⁴ Hollow spheres.

⁵ Spheres filled with smaller spheres.

results are in agreement with Schneider and George [38], who analysed Canadian Delayed coke fly ash by electron spin resonance and found all the vanadium to be in the 5+ oxidation state.

Griffin and Etsell [42] leached as-received Delayed coke ash with a variety of acid and basic leachants and obtained poor vanadium and nickel extractions. The highest extraction of vanadium (about 90%) was achieved by preroasting the fly ash at 900°C in an air atmosphere for 6 hours in the presence of 14wt% NaCl, followed by a 3 hour water leach at 100°C. Roasting with other salts such as potassium chloride, calcium chloride, calcium carbonate and sodium sulphate produced less than 50% extraction. Chlorination roasting of the ashes produced less than 5% vanadium extraction.

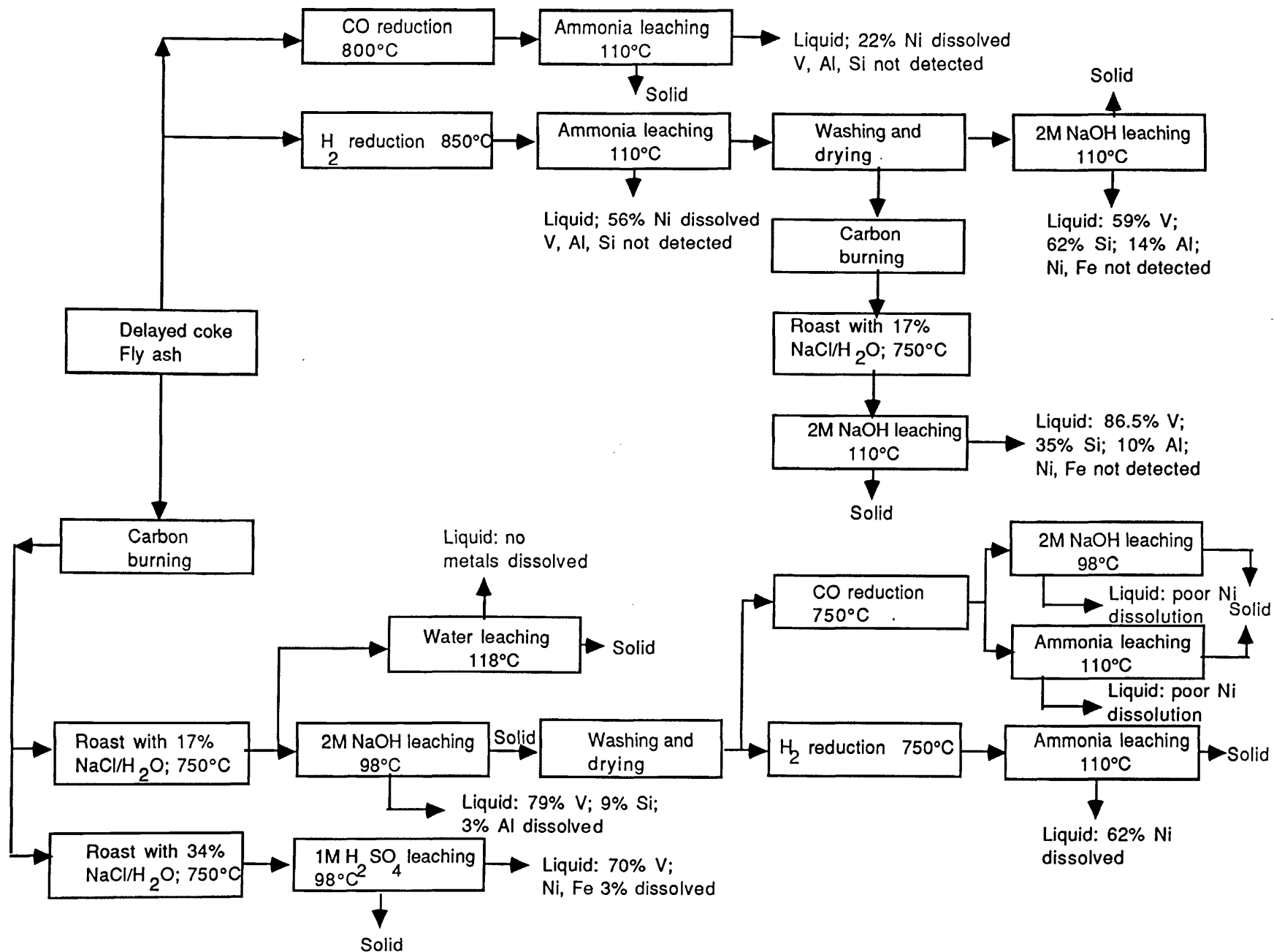
Hanafi and Eid [44] studied the leaching behavior of Egyptian fly ash in alkaline media, and obtained greater than 80%, and almost 98% vanadium extraction by leaching with sodium carbonate and sodium hydroxide, respectively. High leaching temperatures (about 100°C) and long leaching times (6 to 24 hours) were required. Leaching in a 1M NaOH solution gave a higher vanadium extraction than in a 2M solution. This may be due to filtration difficulties caused by the higher viscosity of the more concentrated NaOH solution. The reported vanadium extraction-time curves reached a maximum after 6 hours of leaching, followed by a drop of up to 10%. No explanation is given for this effect.

Burriesci et al [45] found that vanadium can be extracted incompletely, but very selectively, by alkaline leaching of the fly ash. Acid leaching increased the vanadium extraction, but also brought into solution considerable quantities of iron (which exists in greater concentration than vanadium) and nickel. They proposed that vanadium is mainly present as a vanadium (V) species (either V_2O_5 or a vanadate) and some tetravalent vanadium. This proposal arose from their observation of low extraction yields in strong alkaline media, where vanadium (IV)

hydroxide dissolves very slowly, while vanadium (V) is very soluble. Indeed, acid leaching of the residue from alkaline leaching gave mainly vanadium (IV) in solution. Mössbauer spectroscopy analysis of the fly ashes before and after alkaline leaching, revealed that although no iron was dissolved, any iron present as Fe^{2+} was oxidized completely to Fe^{3+} , and the main component of the iron oxide phase was $\alpha\text{-Fe}_2\text{O}_3$. They report no indication from Mössbauer and chemical analysis of the formation of iron-vanadium compounds, which could lower the yield of vanadium extraction by alkaline leaching, and conclude that the presence of iron has no effect on the extraction of vanadium from fly ash.

Gomez-Bueno et al [39] tried a large number of techniques to extract the metal values from Canadian Delayed coke fly ash. Initial experiments with acid leaching (2M acid, 98°C for 25 hours) of the as-received fly ash gave vanadium and nickel extractions of 30% and 25%, respectively. Alkaline leaching increased the yield of vanadium to 55%, and in direct contrast to Hanafi and Eid [44], they found leaching with 2M NaOH to be much more effective than 1M NaOH. The authors then used roasting followed by leaching to recover the metal values. Vanadium was recovered by roasting the fly ash in the presence of sodium chloride and water vapour; nickel values were converted into leachable compounds by using a reduction roasting step. Various flow sheets were devised with this basic approach, as shown in Figure 1.8. Their experimental results are also given in Figure 1.8. The authors concluded that the best experimental route was the NaCl/H₂O roasting of carbon free fly ash at temperatures below 920°C with 5 wt% NaCl to avoid sintering, followed by 2M NaOH leaching at 98°C in an autoclave. Hydrogen was found to be a better reductant than carbon monoxide for nickel. A major problem of their process is that considerable amounts of silicon dissolved after salt roasting (almost 2 moles for every mole of dissolved vanadium, in some cases). Furthermore, the proposed processes are complicated, multi-staged, involve high temperatures and expensive reagents.

Figure 1.8 Several treatment flow sheets for metal recovery from Delayed Coke fly ash [46].



In another work Gomez-Bueno et al [46] characterized the Canadian Delayed coke fly ash and found it to be a mixture of very fine ash particles ($100\% < 22.5\mu\text{m}$) and unburned carbon particles ($>37\mu\text{m}$). The ash consists of spherical particles, some coloured while many were transparent. Cenospheres and plerospheres were also found. A proportion of the cenospheres had microcrystals ($0.1\text{-}0.3\mu\text{m}$ in diameter and $0.5\text{-}5\mu\text{m}$ in length) on both their internal and external surfaces. The microcrystals showed lower silicon, but higher vanadium, nickel, iron and titanium concentrations than that found in the bulk fly ash.

Kostrikin et al [47] revealed a process in which vanadium is recovered from entrained boiler fly ash (which has deposited on heat exchanger). The heat exchangers are regularly cleaned and the waste acidic wash waters, containing the metal values, need to be safely disposed and neutralized. Before neutralization, oxidation with chlorine is performed in order to oxidize sufficient iron to co-precipitate the vanadium. The vanadium rich precipitate is filtered, and the liquid, containing most of the iron and nickel, is further neutralized to precipitate nickel.

Szolnoki [48] obtained extractions of 58% for vanadium and 55% for nickel from the leaching of Hungarian fly ash. A bacterially (*Thiobacillus ferrooxidans*) preoxidized concentrated 9K leaching solution at 50°C during 20 minutes was used. Higher temperatures and longer times produced no increase in the metal yield.

A number of patents have been issued describing processes for the recovery of metals from fly ash, the first of which was issued in 1941 by Noel [61] (an earlier one by Janssen [62] in 1936 only deals with a method to collect the fly ash in order to recover the metal values). He described a process in which the heavy fractions of petroleum are separated from the crude and burned to produce a vanadium-rich fly ash. Most of the patent

relates to the method for burning the heavy oil, but three routes are proposed for recovering the vanadium from the fly ash. One route is the roasting of the fly ash with a suitable fluxing reagent, such as alkali or alkali earth metal carbonates, followed by leaching with water, from which vanadium oxide can be recovered by evaporation. In the second route, the fly ash is treated with fuming hydrochloric acid in the presence of ethanol. The solid residue obtained is then leached with NaOH to dissolve the vanadium values, which are then oxidized with chlorine and precipitated as ammonium vanadate by additions of ammonium chloride. In the third route the fly ash is leached with nitric acid, the leach liquor purified by precipitation of metallic elements, such as lead, by addition of ammonium sulphide, the solution filtered and the filtrate acidified to precipitate vanadium sulphide.

Vojkovic [49] disclosed a process in which the fly ash is preheated to a temperature in the range of 400° to 750°C, under inert conditions, followed by addition of anhydrous sodium carbonate. The inert atmosphere is then replaced by pure oxygen for a few minutes, causing a rapid rise in temperature due to oxidation of residual carbon. If necessary, the roasting process may be repeated after re-grinding the fly ash. Preheating temperatures higher than 750°C are claimed to be detrimental because considerable sintering takes place. The vanadium is then recovered by quenching the hot fly ash in an alkali solution or in water, where the soluble vanadates readily dissolve. Vanadium extractions of 95% or better are claimed. This patent was an extension of an earlier patent [50], with the difference that in this patent the vanadium-bearing material can be fly ash, titaniferous magnetite, vanadium containing slag or ferrophosphorus.

Hahns et al [51] revealed a process in which the fly ash is ground, mixed with over-stoichiometric amounts of alkali carbonates and/or alkali chlorides, and heated in an oxidizing atmosphere to a temperature above its melting point. Sulphur, if insufficient, is added to the mixture in order to form a low

vanadium nickel matte and a low nickel vanadium slag, which are in turn recovered and leached with water to extract the metal values. Vanadium and nickel extractions in the range of 81-91% and 44-96%, respectively, are claimed for different fly ashes.

Tolley et al [52] disclosed a process in which petroleum residues containing vanadium and nickel, the nickel being in the form of a sulphide, are heated to a temperature in the range of 600° to 1500°C, in the presence of a mild oxidizing agent such as carbon dioxide, water vapour, sulphur dioxide or a mixture of these. The treatment converts the nickel sulphide to elemental nickel, which separates from the vanadium oxide. Examples given in the patent revealed the formation of an impure nickel, and of vanadium trioxide. No indication as to the efficiency of the extraction process is given.

Friedman [53] revealed a process to recover vanadium and nickel from fly ash deposited in stack gas scrubber units in coke-fired steam or electricity generators. Two similar routes based on selective precipitation of the metals are proposed. A flow sheet for the process is shown in Figure 1.9. Recoveries of 86% vanadium and 88% nickel are claimed by the first route; and 95% vanadium and nearly 100% nickel for the second route. The second route is however more expensive than the first because of the need to use an oxidant.

A number of similar patents have been issued to recover vanadium from fly ash, and other vanadium-bearing materials, by alkaline leaching. Guillaud [54] disclosed a process in which the fly ash is treated with concentrated sodium hydroxide to selectively solubilise vanadium. The pregnant solution is then treated with calcium oxide to precipitate silica before the vanadium is recovered. Morgan et al [55] claimed to obtain greater vanadium yields by leaching the vanadium-bearing material with aqueous sodium hydroxide, followed by precipitation of vanadium salts by the addition of gaseous ammonia or ammonium hydroxide. Goddard [56] disclosed a

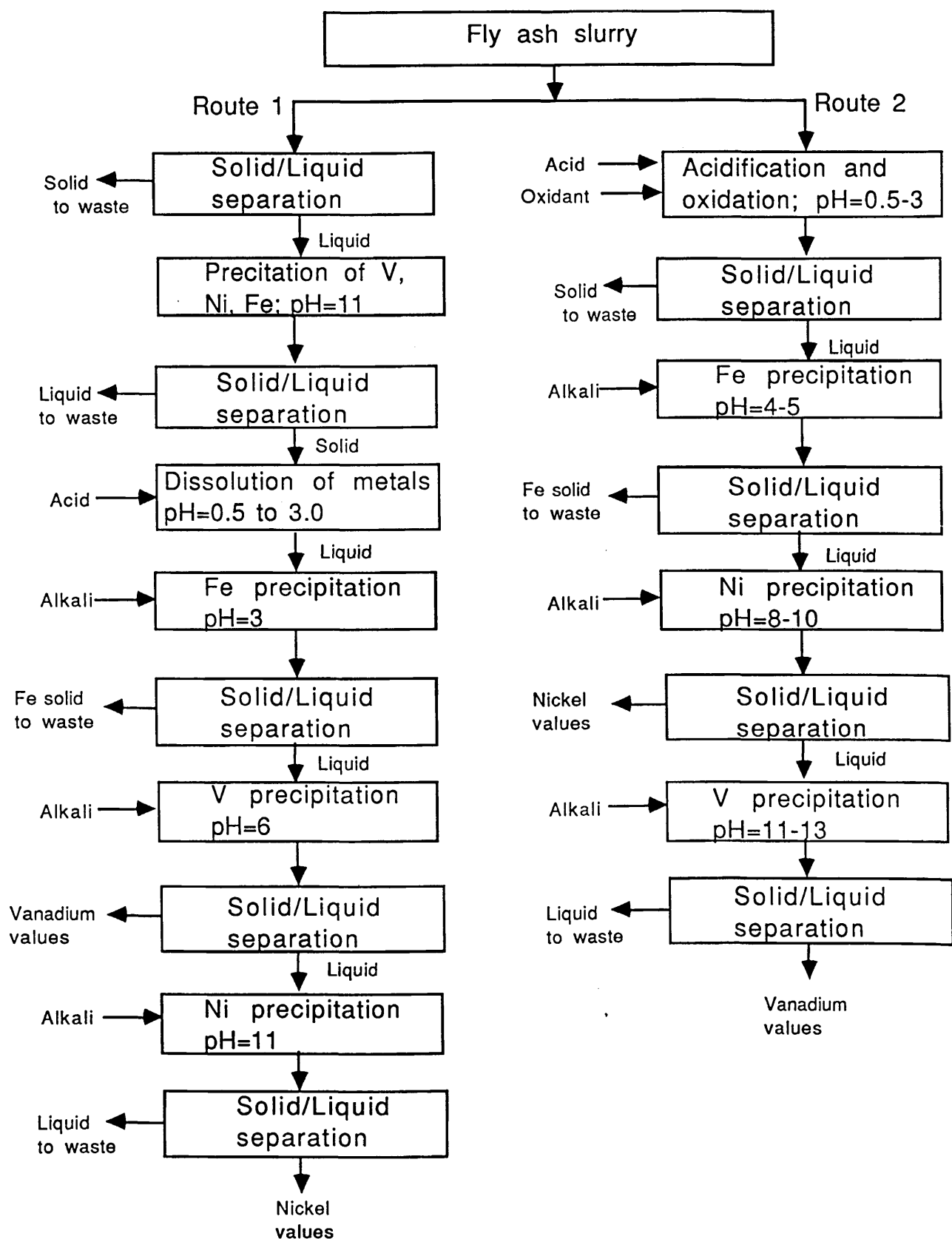


Figure 1.9 Flow sheet for the recovery of vanadium and nickel from fly ash [53]

process in which the fly ash was leached with an aqueous mixture of sodium hydroxide and sodium carbonate (in a ratio ranging from 4:1 to 1:4), at temperatures ranging from 70° to 100°C (the patent extends the temperature range to 300°C, but no examples above atmospheric pressure boiling point were given), in the presence of oxygen. Vanadium recoveries of 81% are claimed, which are three times better than those obtained with pure sodium hydroxide or sodium carbonate solutions.

Hardwick and Patterson [57] described a process in which oil shale ash is roasted at temperatures in the range of 600° to 1100°C, followed by slurrying and carbonate or bicarbonate leaching of the vanadium values. They found that if the ash was left to "condition" in the aqueous slurry before leaching, the vanadium extraction was substantially improved. The best conditions were obtained when the ash was roasted in a fluidized bed furnace at 790°C, followed by slurrying with water at 80°C for 16 hours and subsequent leaching with a carbonate solution. Vanadium extractions of 83% were claimed. Molybdenum present in the ash was also recovered. In another patent, Hardwick and Patterson [58] revealed a process in which the fly ash is roasted at 800°C, slurried and leached at about 55°C by introducing sulphur dioxide gas to lower the slurry pH. Vanadium extractions of 71% were claimed, with low SO₂ consumption.

Nutter et al [59] disclosed a process to recover vanadium from oil shale ashes which contain relatively large concentrations of lime-producing calcium compounds. The ash is mixed with calcium oxide, slurried and heated in an autoclave to 175° to 225°C for 30 to 120 minutes. The slurry is then cooled and the pH lowered by additions of carbon dioxide to solubilise the vanadium values. Vanadium is recovered by extraction with an anion exchange resin (such as a strong base quaternary amine), and latter eluted with a sodium chloride solution. The optimum pH to dissolve vanadium is 6 to 7.5. Addition of CO₂ also precipitates calcium carbonate, which is roasted to provide the

calcium oxide for the leaching stage and the CO_2 for pH control. Vanadium extractions of the order of 54% are claimed. The process can be further improved [60], to yield 65% vanadium, if the anionic resin is added to the slurry before CO_2 addition, to shift the dissolution equilibrium.

1.3.2 b) Metal extraction from petroleum cokes.

Jack et al [41] investigated the extraction of vanadium and nickel from Canadian Flexicoke by a leaching technique. Most of the work was conducted at ambient temperature, in an airlift percolator to simulate heap leaching conditions. Extraction curves for vanadium with different leachants are shown in Figure 1.10. Leaching with 1M sulphuric acid readily extracted vanadium, and the leachate acquired a blue colour characteristic of vanadium in the +4 oxidation state. Initially, there was a rapid increase in vanadium extraction, but the rate dropped off after a week. Acid leaching gave the best results, especially for ground coke.

In alkaline solutions, aerial oxidation of vanadium (IV) is rapid [62] and consequently vanadium was extracted in the 5+ oxidation state. Alkaline leaching extracted only half the vanadium extracted by acid leaching, but the selectivity was better (as at high pH iron and nickel both form insoluble hydroxides). Addition of complexing agents such as EDTA considerably improved the vanadium extraction and solubilised some iron and nickel.

Extraction curves for nickel with a variety of acidic leaching agents are given in Figure 1.11. Nickel was extracted to a greater extent than vanadium, and a considerable proportion of the nickel content was readily extracted under very mild conditions. Within a week, water leaching (pH 4-6) extracted about 20% of the total nickel. Jack et al speculate that a considerable proportion of the total nickel is present in Flexicoke in a simple ionic form; in the water leachate, sulphate was found as the counterion in a molar ratio of 1:1 with nickel.

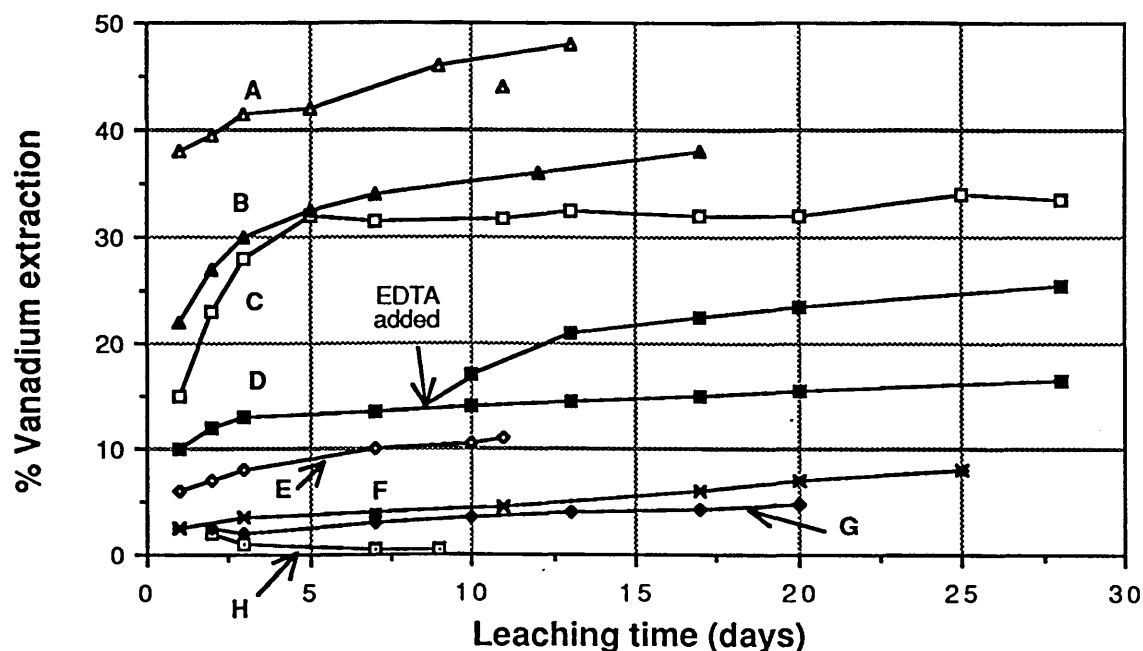


Figure 1.10 Vanadium extraction from Flexicoke [41].

A=1M H_2SO_4 , ground coke; B=2M HCl , as-received coke; C=1M H_2SO_4 , as-received coke; D=5% $\text{NaHCO}_3/\text{Na}_2\text{CO}_3$, as-received coke; E=1% $\text{NaHCO}_3/\text{Na}_2\text{CO}_3$, as-received coke; F=1M H_2SO_4 re-leached ground coke; G=sodium acetate, pH=6; H= H_2SO_4 , pH=2.

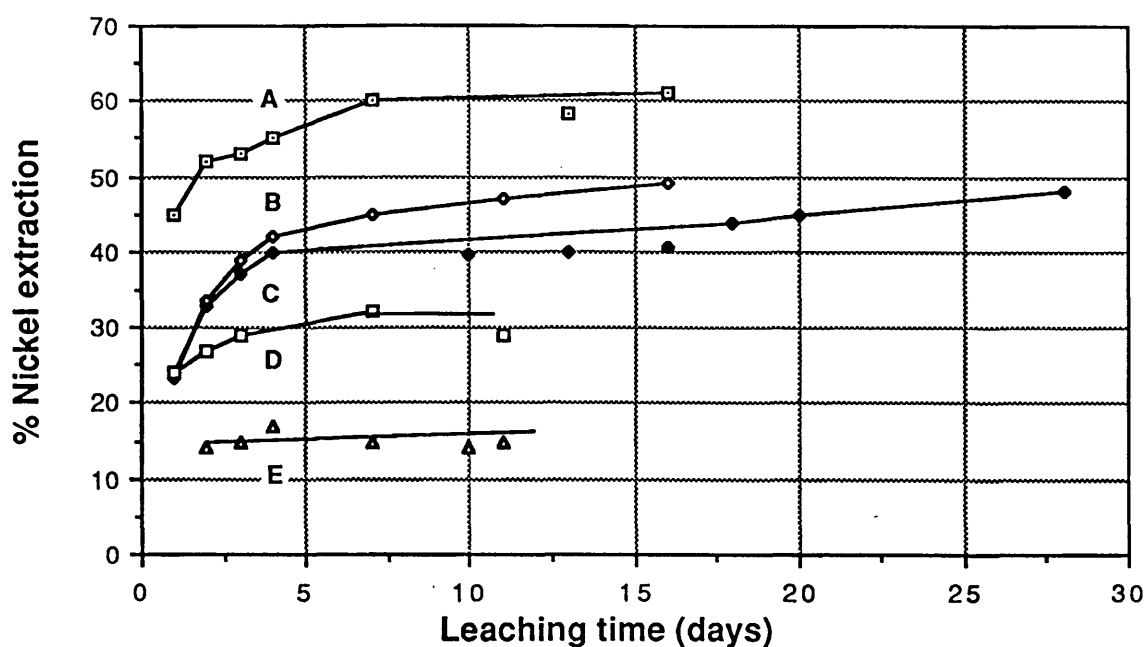


Figure 1.11 Nickel extraction from Flexicoke [41].

A=1M H_2SO_4 , ground coke; B=2M HCl , ground coke; C=1M H_2SO_4 , as-received coke; D=1M H_2SO_4 , pH=4; E=sodium acetate, pH=6.

Enhancement in both the vanadium and nickel extractions were found by increasing the salt concentration, or by adding redox reagents, to the leaching solutions. This increase appeared to be associated with ionic effects, rather than complexation or redox effects.

Increases in temperature considerably enhanced the metal extraction from acid leaching of Flexicoke, as shown in Figure 1.12 below. Lower pH also improved the metal release.

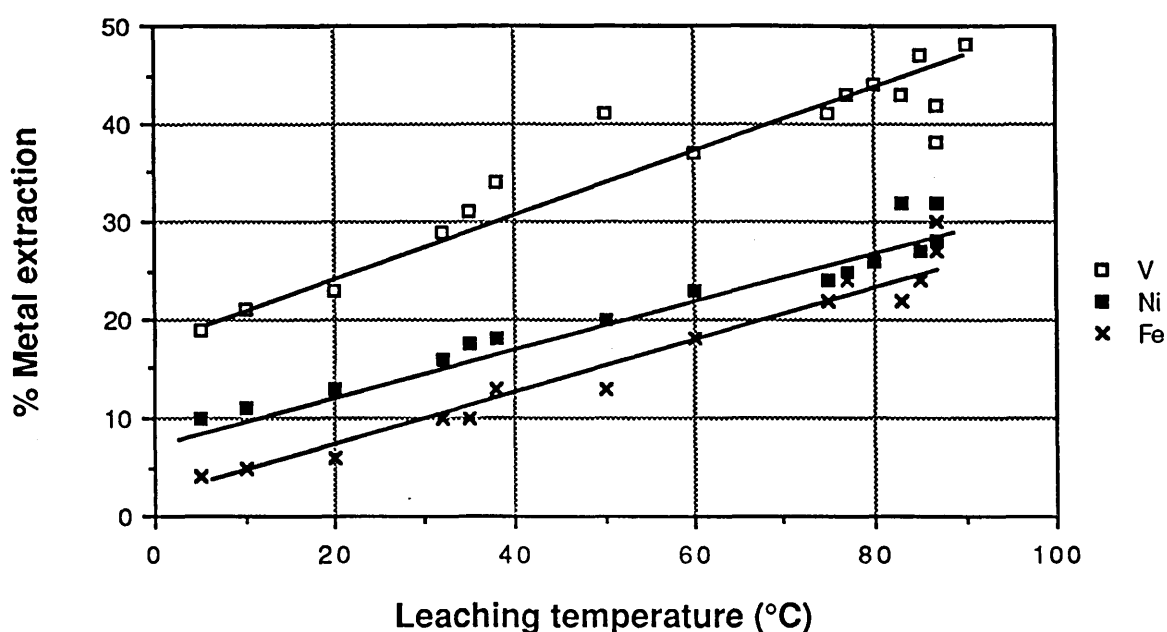


Figure 1.12 Effect of temperature on the metal extractions from leaching of Flexicoke for 2 hours [41].

Iron and titanium were co-extracted with vanadium and nickel during acid leaching. The extraction behaviour of iron closely resembled that of vanadium and the authors suggested that both metals may occupy similar sites in the coke. Colorimetric analysis of the leachant showed that about 80% of the extracted iron is in the ferrous state. Titanium constitutes only a minor component of the acid leachate; furthermore, it was poorly extracted (12-20%).

In a more recent work, Jack et al [63] report the metal extraction from the leaching of Flexicoke, Delayed coke and Fluid coke. They found that under the same conditions greater metal recoveries were obtained from Flexicoke than from Delayed coke or Fluid coke. This has been confirmed by Rodriguez [64] using Venezuelan Flexicoke and Delayed coke. Jack et al found that that Delayed coke was particularly intractable to leaching, and suggested the difference in leaching behaviour among the various cokes was due to differences in specific surface areas, to the non-wettability of the Delayed coke particles and to differences in the chemical nature of the metals in the various cokes. The addition of surfactants failed to increase the metal extraction. Therefore, the difference in leaching behaviour of the various cokes is probably due to differences in the metal species. Indeed, Flexicoke, which is the most amenable coke to leaching, has a much lower heteroatom to metal ratio than the other cokes.

Schneider and George [38] also performed acid leaching (2M HCl for 2 hours at 85°C) on Canadian Delayed coke, and obtained only 3% vanadium and 2% nickel extraction.

Jack et al [63] also attempted halogenation of Delayed coke as a method to extract the metal values. Chlorination at 250° to 520°C were performed, but the metal yields were low (7.6% V, 1.9% Ni, 15% Fe). Increases in temperature decreased the metal extractions. Undesirable by-products were obtained (such as hexachlorobenzene). Chlorination and bromination of the cokes suspended in CCl₄ was also attempted, with equally poor results

Microbial assisted leaching of Flexicoke and Delayed coke with *Thiobacillus ferrooxidans*, by the same authors [63, 65], yielded a moderate increase in the metal extraction from Flexicoke, as compared to acid leaching. The results for Delayed coke were not reported, although it is claimed that better microbial growth is obtained with Delayed coke, probably due to its higher sulphur content.

A number of patents have been issued for processes to recover metals from petroleum cokes. The earliest patent found was that by Oberle and Scofield in 1924 [66] and its continuation in part in 1927 [67]. The process consists of burning the petroleum coke and collecting the fly ash in a suitable absorbing material, such as bauxite and colloidal clays. Vanadium is then dissolved from the absorbing material by using a suitable solvent. No more details or examples are given by the inventors.

Vessely [68] revealed a process in which sulphur-containing petroleum cokes are roasted in an oxidizing atmosphere in the presence of a salt, preferably sodium chloride. The preferred temperature range is 800° to 850°C, with at least 10% excess of NaCl, and preferably 40 to 80%, over that required to convert all the nickel and vanadium to nickel chloride and sodium vanadate (assuming that nickel and vanadium are in the form of NiS and V₂S₃). The metal salts are dissolved in SO₂ saturated water at 80° to 95°C, and sulphuric acid added to maintain the solution pH below 3. Under these conditions V₂O₅ precipitates, and is recovered by filtration. The filtrate is then treated to remove dissolved SO₂ by blowing air, the pH raised with ammonia additions, and CO₂ introduced to precipitate nickel as nickel carbonate. Temperatures in the range of 120° to 180°C, and pressures of 200 to 500 p.s.i. are used. The nickel carbonate is then calcined in air at 540°C to produce nickel oxide.

Two processes were patented by McCorriston in which the cokes (or fly ash) were roasted in an oxidizing atmosphere in the presence of a carbonate salt [69, 70] or a sulphate salt [71]. Both processes are otherwise identical. The temperature range for the roasting operation is 500° to 880°C, for 0.2 to 5 hours, with an amount of salt which is insufficient to react with more than 10% of the sulphur contained in the coke (or fly ash). The resulting solid material is then leached with water at 60° to 100°C to dissolve the contained vanadates. The leachant pH is then raised with ammonia and vanadium precipitated as

ammonium metavanadate. Vanadium recoveries of 86% from Flexicoke, 96% from Delayed coke and 88% from Delayed coke fly ash are claimed by the carbonate process. The sulphate process gave lower yields of 67% and 71% for Delayed coke and Delayed coke fly ash, respectively.

Hass and Hess [72] issued a patent in which the petroleum cokes are gasified in the presence of an alkali metal salt, preferably sodium carbonate, to produce a hydrocarbon gas stream and a residue containing water soluble alkali metal vanadates. The gasification reaction is carried out in a fluidized bed reactor, with steam at a pressure of 10 to 300 p.s.i. and temperatures of 540° to 1100°C. The resulting solid is leached with water at 25° to 95°C to dissolve the vanadates, and vanadium recovered either by solvent extraction (after increasing the pH of the leachate) with a tertiary or quaternary amine, such as Alamine 336, or by precipitation with ammonia. Vanadium recoveries of 99% are claimed from Canadian Fluid coke.

Goddard [77] disclosed a process in which vanadium ores are roasted at a temperature of 800° to 850°C, in an oxidizing atmosphere in the presence of sodium chloride and a carbonaceous material, preferably Flexicoke. The inventor found that the extraction of vanadium from the ore was considerably improved if vanadium was present in the carbonaceous material, even if 100% vanadium extraction from the coke was assumed. In another patent, already reviewed in Section 1.3.2 (a), by the same inventor [56] alkaline leaching was used and vanadium extraction of 73% was claimed from Flexicoke.

Queneau [78] revealed a process in which vanadium and nickel are recovered from a coke slurry (formed by petroleum coke and aqueous sodium carbonate) by digesting the slurry at a moderately elevated temperatures (250°-320°C) in a pressurized autoclave under an oxygen overpressure. A liquor pregnant in V_2O_5 is obtained and separated from the digestion residues. The residue is subsequently selectively leached to recover nickel. Extractions of vanadium of 99% are claimed, but

no data is given for nickel. Steam is also recovered by the process. In a similar process Sit [79] subjects the petroleum cokes (or carbonaceous fly ash) to an oxidative leach in an autoclave at 250° to 340°C, and pressures of 1000 to 4000 p.s.i., while maintaining the pH of the leachant below 1, to produce steam, and a pregnant liquor containing the vanadium and nickel. After filtration the metals are recovered by precipitation. Vanadium and nickel recoveries greater than 90% and 60% are claimed.

Schemel et al [74] revealed a leaching process for recovering vanadium and nickel from Venezuelan Flexicoke. The coke is subjected to an oxidative acid leach for four hours at 20° to 90°C (preferably at 80°C). The leachant should preferably contain some dissolved vanadium. The pregnant liquor is then filtered, and its pH raised to 5.5 to 6.5 to recover vanadium in the trivalent and tetravalent state. After solid/liquid separation the pH of the leachant is again increased to 8.5 to 9.5 to precipitate nickel. 99% vanadium extraction is claimed, but the inventors do not give the particle size of coke used, and an exceptionally rich Flexicoke containing 15.52 wt% vanadium was used (the norm being 1 wt% or less). No data is given on the nickel extraction efficiency.

Fletcher and Holm [80] have issued a process for the simultaneous production of hydrogen and the vanadium and nickel values. The cokes are roasted at a high temperature (420° to 730°C) in an oxygen and steam atmosphere to form a hydrogen and carbon monoxide mixture. Potassium carbonate may be used as a catalyst. The metals and K_2CO_3 are then recovered from the roast residue, but no details are given of the method to be employed.

1.3.3 OTHER USES FOR PETROLEUM COKES.

The most obvious use for petroleum cokes is as a solid fuel, and as such they have been used for a long time. Metal extraction

from the ash residue obtained after burning the cokes has been attempted as already discussed in Section 1.3.2 (a). The advantages of using petroleum cokes instead of coal as a solid fuel are (a) easy storage; (b) higher heating values; (c) lower ash content; (d) lower burning rates. Gray and Pesek [81] recently reviewed the use of petroleum cokes as an alternative to coal. Traditionally cokes containing greater than 4 wt% sulphur have been used as solid fuels. The burning characteristics of petroleum cokes are similar to those of anthracite, with Delayed coke being the easiest coke to burn. A problem experienced in steam generation is carryover of vanadium pentoxide to the convection section, where it promotes the conversion of some SO_2 to SO_3 and leads to corrosion problems.

An attractive use for petroleum cokes is their gasification into valuable CO and H_2 gas mixtures. A number of processes have been proposed. The process described by Fletcher and Holm [80] has already been reviewed in Section 1.3.2.b. Other developed gasification processes have been either converted or being converted for the use of petroleum cokes [82]. In the Texaco process a coke-water slurry is gasified at temperatures in the order of 1260° to 1500°C, and pressures of 40 to 80 atmospheres, to convert 90 to 99% of the carbon into gas. Synthesis gas containing 34.5% H_2 , 45.2% CO, 19.2% CO_2 , plus small amounts of H_2S and COS, have been obtained from the gasification of Delayed coke. In the Rockwell process the coke is gasified in a molten bath of sodium carbonate at 950°C and 30 atmospheres in the presence of oxygen and steam. The sulphur and metals in the coke remain in the melt. Vanadium is recovered by water leaching of spent sodium carbonate. This process is claimed to be particularly attractive for low reactivity cokes such as Flexicoke. Other commercial processes such as the Lurgi Slagging process and the Lurgi Dry Ash process are being tested or modified to use petroleum cokes as the feed material [82].

Petroleum cokes have also been used to produce anodes for the electrochemical industry. The production of aluminium by the

Hall-Heroult process requires about 0.45 kg of carbon for every kilogram of aluminium produced; the carbon is used in the form of consumable anodes. About 80% of the carbon for Hall-Heroult cell anodes is calcined petroleum coke; the remaining carbon is coal tar pitch used to bind the coke particles. 99% of all the petroleum coke used by the electrochemical industry is used for aluminium electrolysis. Other uses are in the chlorine, magnesium, sodium, lithium, sodium chlorate and steel (only Delayed coke) industries. Although a considerable amount of petroleum coke is produced, only a small portion of it is suitable for Hall-Heroult process anode production. Much of the coke produced contains excessive quantities of iron, nickel, vanadium and silicon. Excessive sulphur also makes coke unsuitable from an environmental point of view, since sulphur-containing gases are evolved during electrolysis. Moreover, coke porosity may be too low resulting in poor quality anodes. Table 1.5 gives the typical specifications for calcined petroleum cokes in the Hall-Heroult process [83].

Particle size (cm)	2.54 maximum
Bulk density (Kg/m ³)	800 minimum
Real density (Kg/m ³)	2030 minimum
Moisture (wt%)	0.5 maximum
Volatile matter (wt%)	0.5 maximum
Ash (wt%)	0.5 maximum
Silicon (wt%)	0.05 maximum
Iron (wt%)	0.03 maximum
Vanadium (wt%)	0.045 maximum
Nickel (wt%)	0.04 maximum
Sulphur (wt%)	3.0 maximum

Table 1.5 Typical specifications for calcined petroleum cokes [83].

The vanadium content of the cokes is particularly important. Houston [84] in his review of anode consumption in the Hall-Heroult process points out that an increase in vanadium concentration from 0 to 0.1% decreases the current efficiency by about 11%. This is due to the various oxidation states of vanadium, leading to current being spent in oxidation-reduction cycles. However, the use of Canadian Fluid coke containing about 4000 ppm has been reported [34] (although Fluid coke presents some difficulties in anode manufacture). Furthermore, vanadium and V_2O_5 are both effective catalysts for graphite (anode) oxidation, specially at around 550°C which is well within the temperature range experienced by the anodes. Nickel is also an oxidation catalyst of moderate to weak strength, but its effect is worse in the presence of vanadium. Table 1.6 presents a list of common impurities found in anodes and their effect on the air oxidation of graphite.

Inclusion	Effect	Inclusion	Effect
Si, SiO_2	MC	Fe, Fe oxides	M-WC
V, V_2O_5	SC	Ni	M-WC
Na, alkali salts	SC	S	WC-N
Ca	WC	Pb, Pb oxides	SC
Cu, Cu oxides	SC	Zn	WC
Cr	M-WC	Ti	WC
AlF_3	I	Al, Al_2O_3	M-WC
B, B_2O_3	I	P, Phosphates	I

Table 1.6 Effect of impurities on the air oxidation of graphite [84]. C=catalyst; S=strong; M=moderate; W=weak; N=no effect; I=inhibitor.

The fairly low sulphur content of Flexicoke could make it a useful material in ferrous metallurgical processes. Petroleum cokes are reportedly already being used to make metallurgical grade coke [23]. In order to be used as part of the burden to a blast furnace, small coke particles (such as those obtained from fluidized bed processes) need to be pelletised into coarse and strong aggregates to prevent them from being carried out of the burden before reacting. An interesting alternative is to inject the cokes into the tuyeres of the blast furnace. Flexicoke and Fluid coke have a particle size distribution which can be easily transported in a pneumatic system, without the need for sizing and grinding. The low volatility of Flexicoke should reduce problems associated with solids injection in this very high temperature zone [23].

1.4. THE SEGREGATION PROCESS.

1.4.1 INTRODUCTION.

The segregation process involves the heating of an ore in the presence of a chloridizing agent and a carbon source. By a complex series of reactions the valuable metal in the ore reacts with the chloridizing agent, is transported in the vapour phase as a chloride and deposits on the carbon source where it is reduced to the elemental form. Any metal that can form volatile chlorides and oxychlorides (e.g. Cu, Ni, V, Fe, Sb, Bi, Co, Ag, Au, Pb, Pd, Sn, Ti, etc) is potentially amenable to treatment by the segregation process [85, 86]. The process was discovered by accident in 1923 by Moulden and Taplin who found that by heating a copper ore from Sogasca, Chile, with coal at 600° to 800°C, the copper was not reduced *in situ*, but migrated and deposited on the coal surface. This anomaly was explained by the presence of sodium chloride in the ore. Any halide was found to be a segregating agent. The process has attracted most interest for the recovery of copper from refractory ores and a number of commercial operations have opened.

Patents were issued [87] soon after the discovery of the process. The first pilot plant, to recover copper, was opened in 1929 at the Alaska mine in (the then) Southern Rhodesia. It operated until 1931 when the low price of copper forced the mine to close. The Union Miniere du Haut Katanga plant (in the then Belgian Congo) [87] operated with difficulties from August to November 1931, but the low price of copper also forced it to close. No plants operated for twenty seven years, until 1958 when a pilot plant opened in Maunitania to treat the gold-bearing Akjoujt copper ore [88]. This plant closed down due to operating difficulties associated with the two stage process used. The operating problems were overcome by Transarizona Resources in Lake Shore, U.S.A. [89] who in 1960 used a one stage rotary kiln. In the same year a shaft furnace was constructed at Berenguela Mine, Peru [90] to treat a silver-copper ore. The Anglo American Corporation built a pilot plant in 1967 in Rhokana, Zambia [91] which incorporated an outer fluidized bed heating reactor from which hot ore was transferred to a central segregation chamber into which the reactants were added. A full commercial plant was then opened in 1971 in Akjoujt mines, which ran successfully. All plants have now closed down for economic reasons.

The segregation of nickel from refractory nickel ores (laterites) has also attracted considerable interest, although no commercial operation has opened to date. The largest operation has been a 1 metric ton of ore per hour pilot plant operated by Minpro-Pamco in Sweden in 1981 to 1983. They employed a rotary mechanical kiln in which the grinding and segregation reactions took place in the same vessel. The heat for the reactions was provided by the heat from the comminution operation. Laboratory and small pilot plant work has also been conducted by Fuji Iron and Steel, Japan [95] and by Ser and Stojic from the Rudarski Institute, Yugoslavia [96]. The Anglo American Corporation reportedly [85] has facilities for pilot-scale (ten-tons per day) nickel segregation investigation in their laboratories in Johannesburg.

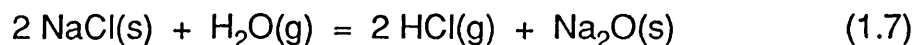
The mechanism for nickel segregation bears close resemblance to that of copper segregation proposed originally by Rey [97]. He divided the process into three major steps:

- (a) The production of the chloridizing gases.
- (b) The formation and volatilization of the valuable metal chloride.
- (c) The precipitation of the reduced metal on the carbon surface.

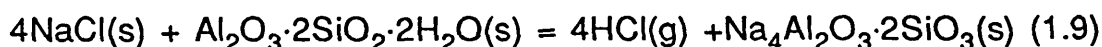
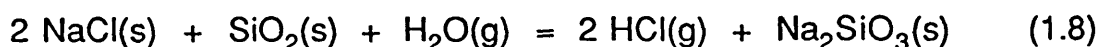
The segregation process will be described in the following sections using these three headings; emphasis will be placed on nickel segregation.

1.4.2 THE PRODUCTION OF THE CHLORIDIZING GASES.

It is generally recognized that the actual chloridizing agent during the segregation roasting of an ore is hydrogen chloride gas, which is produced by the action of moisture on sodium chloride (reaction 1.7):

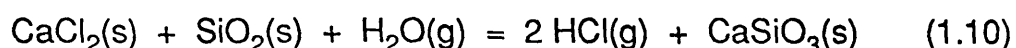


Rey [97] first proposed the salt-quartz reaction (reaction 1.8) claiming that better HCl yields could be obtained over those from reaction (1.7); however, Rampacek et al [98] showed that the yield of HCl from reaction (1.8) was not greater than that from reaction (1.7) in the presence of moisture. They also found that the clay minerals play an important part in the production of HCl, owing to the release of water upon heating to 750°C (reaction 1.9). When the clays were calcined at 1000°C prior to segregation no HCl was formed upon subsequent heating with salt at 750°C.



The high temperature hydrolysis of sodium chloride in the presence of silica has been investigated by Hanf and Sole [99]. They showed that although the thermodynamics of reaction (1.8) appeared to be unfavourable, the sodium silicate product is soluble in the silica reactant and thus the activity of this product is very low. This results in the generation of considerable quantities of HCl, in contradiction to the work of Rampacek et al [98]. Hanf and Sole also found that the hydrolysis reaction was fast, and that the equilibrium partial pressure of HCl was established almost instantaneously at typical copper segregation temperatures (700° to 850°C).

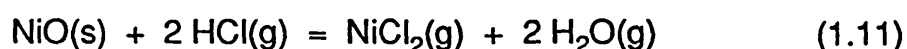
Nickel oxide ores can also be segregated using NaCl as the chloride source, but it has been found that calcium chloride is the most effective reagent. It is usually assumed that the mechanism for HCl generation with CaCl_2 is similar to that shown in reaction (1.8) for NaCl, and some direct evidence for reaction (1.10) below is available. It is not completely clear why CaCl_2 is more effective than NaCl, but one reason is that CaCl_2 can provide higher HCl partial pressures for a given water vapour pressure [85, 86], as shown in Table 1.7 below.



The role of water in the generation of HCl from CaCl_2 in the presence of clay minerals is uncertain, because at the temperatures required for nickel segregation (950° to 1050°C) water vapour should be in short supply due to the almost complete dehydration of the clay minerals above 800°C [85].

1.4.3 FORMATION OF THE NICKEL CHLORIDE SPECIES.

The chlorination reaction of nickel oxide ores is generally believed to be that shown by reaction (1.11) below.



Kellogg [100] calculated the free energy for reaction (1.11) as +0.2 kCal/mol at 1000°C, showing how marginal the thermodynamics of the nickel segregation process are. Iwasaki [86] found from thermodynamic calculations that the HCl partial pressure required for nickel segregation is several orders of magnitude greater than required by copper segregation. Hence the requirement for CaCl₂ as the chloridizing reagent in the previous step. Higher temperatures are also required, typically in the order of 900° to 1050°C.

Reaction	Temperature (°C)	pH ₂ O	log pHCl
(1.8)	750	0.3	-2.71
		0.03	-3.21
	950	0.3	-1.79
		0.03	-2.29
(1.10)	750	0.3	-0.59
		0.03	-1.09
	950	0.3	-0.21
		0.03	-0.71

Table 1.7 Effect of temperature and water vapour partial pressure on the equilibrium partial pressure of HCl produced by reactions (1.8) and (1.10) [86].

Iwasaki [86] also found that the stability fields of iron and nickel chloride at 950°C (as a function of the partial pressure of HCl, H₂ and O₂) overlap so closely that it is surprising that nickel segregation in the presence of iron is at all possible, Figure 1.13. Indeed, Turkdogan [101] found that the partial pressure of FeCl₂ is higher than that for NiCl₂ at all temperatures between 600° and 1000°C, and for both salts NaCl and CaCl₂, Figure 1.14.

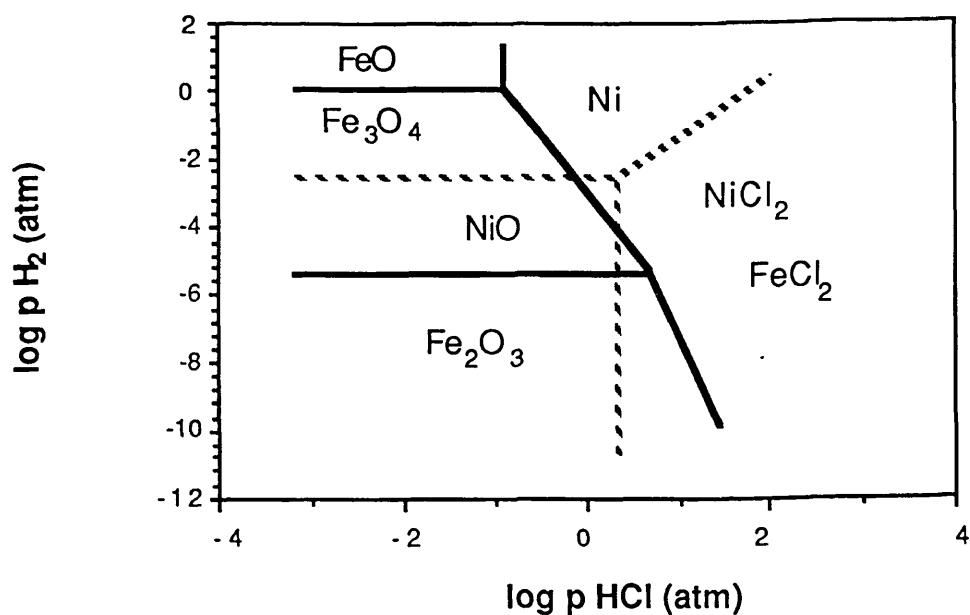


Figure 1.13 Equilibrium diagrams for Fe-H₂-HCl (solid line) and Ni-H₂-HCl (broken line) at 950°C [86].

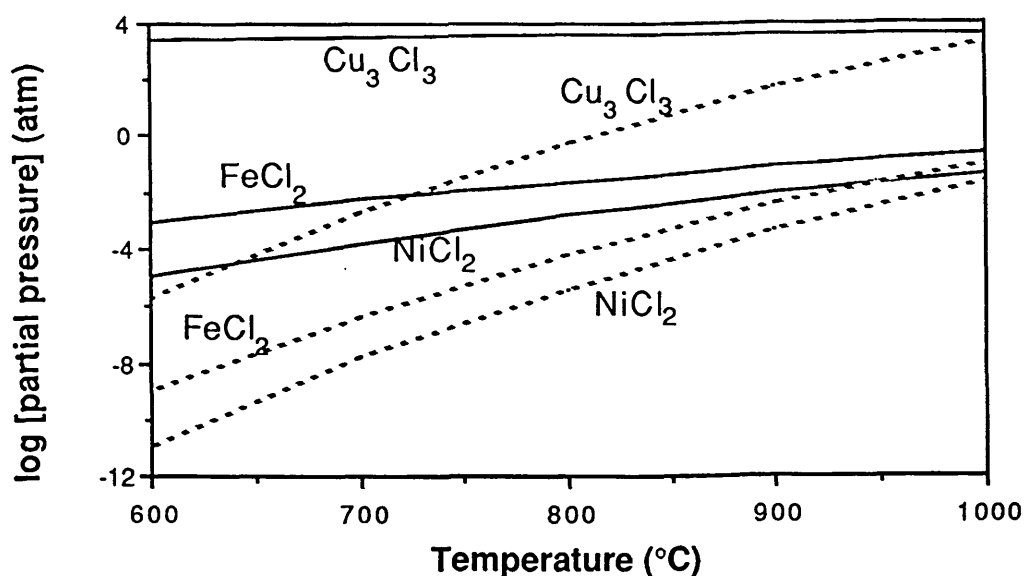


Figure 1.14 Equilibrium partial pressure of metal chlorides over their oxides and with $p^2_{\text{HCl}}/p_{\text{H}_2\text{O}}$ ratio set by the salt-silica-water vapour equilibrium [101]. CaCl₂-SiO₂ equilibrium (solid lines); NaCl-SiO₂ equilibrium (broken lines).

A more detailed stability field diagram [86] for the Ni-H₂-HCl system is given in Figure 1.15. It should be noted that the equilibrium partial pressure of nickel chloride vapour (538 mm Hg at 950°C) may not be attained in full at a water partial pressure of 0.3, since the total pressure of the ore bed would not be too much higher than one atmosphere. The partial pressure of NiCl₂ vapour with CaCl₂ at 950°C was calculated to be 17 mm Hg. Since changes in the water vapour partial pressure shifts the equilibrium line between the nickel oxide and the chloride, it appears that the lower the water vapour partial pressure, the lower the HCl partial pressure required to chloridize NiO, and hence the less quantity of additives required.

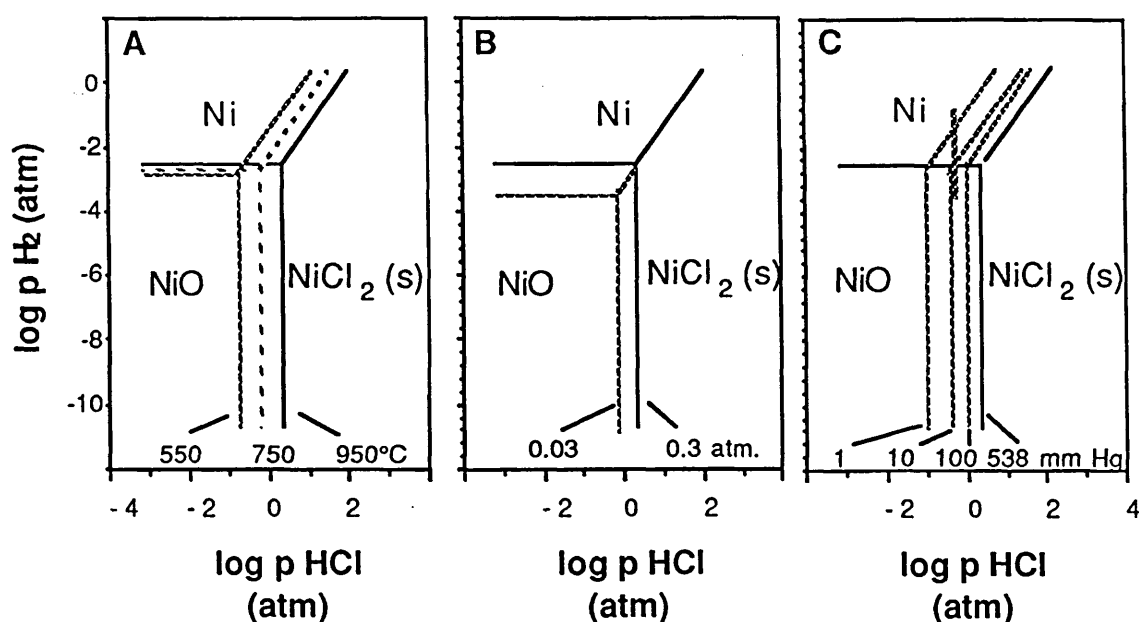


Figure 1.15 Equilibrium diagrams of Ni-H₂-HCl system [86]. (A) Effect of temperature, pH₂O=0.3 atm; (B) Effect of water vapour pressure at 950°C; (C) Vapour pressure of nickel chloride at 950°C and pH₂O=0.3 atm. (shaded region indicates pHCl over CaCl₂-H₂O-SiO₂)

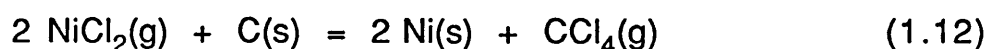
Brittan and Lidenberg [102] found that extraction of nickel from oxide ores using hydrogen chloride gas alone was sluggish, but the reaction was promoted by the presence of calcium chloride

and reducing conditions. Apparently, calcium chloride promotes certain mineralogical changes which render the oxide more amenable to chlorination. They also found that the chlorination reaction (reaction 1.11) was the rate controlling reaction of the segregation process. On the other hand, Marples [103] and Turkdogan [101] believe the rate controlling step for the process to be the generation of hydrogen by reduction of water vapour with carbon on which the metal deposits, Section 1.4.4.

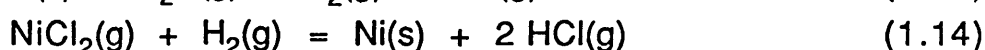
Unlike copper segregation, nickel was found to volatilize as the monomer. No evidence of polymerization has been found. For copper segregation, Hadjiat and Richardson [104] and Gross and Stuart [105] reported that complex gaseous molecules (mainly NaCuCl_2 and NaCu_2Cl_3) contribute considerably to the transport of copper. Hadjiat [104] found no such complexes for the NiO-CaCl_2 reaction, and report only NiCl_2 as the nickel vapour species above the ore-salt mixture.

1.4.4 REDUCTION OF THE NICKEL CHLORIDE.

In the segregation process of both copper and nickel ores the metallic phase precipitates mainly on the surface of a carbon reductant. However, carbon is thermodynamically unable to reduce the metal chlorides, i.e. for nickel, reaction (1.12) has a free energy of formation of +8 and +52 kCal/mol at 100° and 1000°C, respectively.



In the presence of a small amount of water vapour, carbon will react to form hydrogen, which is generally considered as the reductant in the segregation process. Mimura et al [106] showed that NiCl_2 could be reduced with hydrogen at temperatures above 340°C, but not by carbon monoxide in that temperature range. The reactions are assumed to proceed in the following manner:



From Figure 1.15 (c) the isobars of nickel chloride vapour over metallic nickel are seen to have a positive slope, indicating that the partial pressure of the NiCl_2 vapour decreases with increasing hydrogen partial pressure. In nickel segregation mildly reducing conditions prevail and relatively high hydrogen concentrations have been reported [85].

The reduction of nickel chloride vapour is more complicated than that for copper chloride, because of the higher HCl partial pressures used. Under these conditions FeCl_2 can readily form, and with the low water vapour partial pressure, higher temperatures and reducing conditions, iron can segregate with the nickel. It has, however, been noted that NiCl_2 is more easily reduced than FeCl_2 [85]. Studies of the metal blobs deposited on carbon samples have shown them to consist of a Ni-Fe alloy containing between 40 and 70% Ni [85, 86].

The presence of carbon is essential to the process, since it provides nucleation sites for nickel precipitation, and a controlled release of hydrogen. The more reactive the carbon the easier the precipitation reaction takes place. Thus, coal is better than coke, char or charcoal. Graphite has been found to be totally ineffective.

1.4.5 CHLORINATION OF VANADIUM ORES.

As early as 1906 Hardy [107] issued a patent for extracting vanadium by roasting the vanadium-bearing ore in the presence of NaCl , or other chloride salt, to form a water soluble sodium vanadate. The salt roasting of vanadium ores has been extensively reviewed by Goddard and Fox [108]; salt roasting of vanadium-containing fly ash has already been reviewed in Section 1.3.2. Under all roasting conditions the emission of HCl or Cl_2 gas has been observed, but no author reports the vapour transport of a vanadium chloride or oxychloride. Evidently, the

formation of the vanadate salt is more favourable than the chlorination and volatilization reaction.

Vanadium chlorination has been practiced as a means to produce metallic vanadium. The chlorination of ferrovanadium and V_2O_5 has been reviewed by Gupta [109], who summarized the chlorination-purification-reduction routes investigated for the production of vanadium by means of the flow sheet shown in Figure 1.16. The vanadium source for chlorination is either ferrovanadium or V_2O_5 (in the presence of carbon), which are processed to produce either VCl_3 or VCl_2 . These chlorides are then subjected to reduction with magnesium to produce vanadium sponge. Sodium may also be used.

The thermodynamics of chlorination of vanadium oxides and the general chemistry of vanadium chlorides and oxychlorides are reviewed in Chapter 5, Sections 5.1 and 5.2.

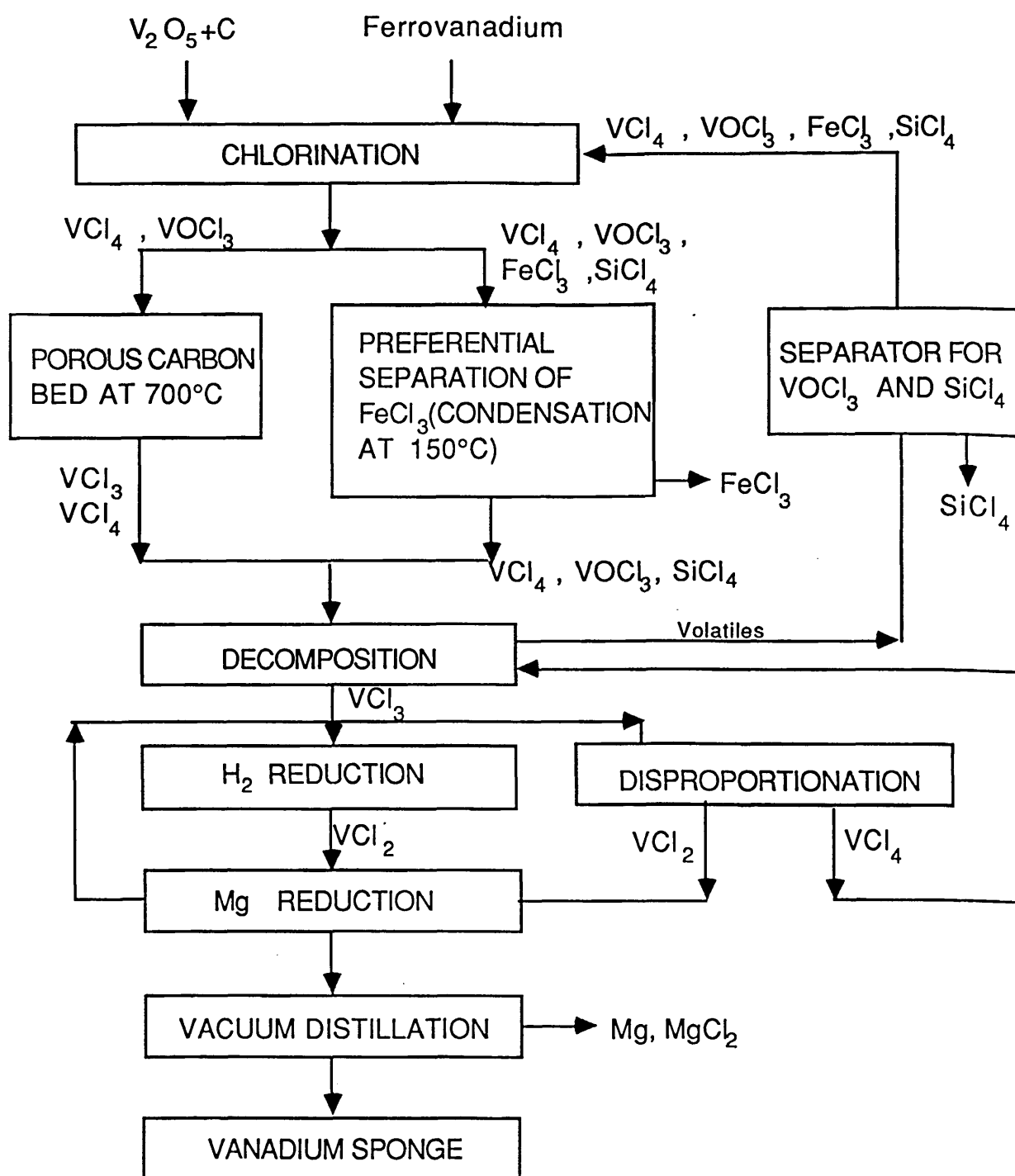


Figure 1.16 Preparation of elemental vanadium by chloride metallurgy [109].

2. EXPERIMENTAL PROCEDURE.

2.1 MATERIALS.

Both Flexicoke and Delayed coke were supplied by Intervep S.A., Los Teques, Venezuela. The Flexicoke was produced at Lagoven S.A. petroleum refinery at Amuay in western Venezuela, whilst the Delayed coke was produced at Intevep S.A. pilot plant at El Jobo, eastern Venezuela.

The following materials were used in the experimental work:

1. Standard solutions for atomic absorption spectrophotometry:

- a) Vanadium, B.D.H. Spectrosol, 1000 μ g/ml in 1% HNO₃.
- b) Nickel, B.D.H. Spectrosol, 1000 μ g/ml in 1% HNO₃.
- c) Iron, B.D.H. Spectrosol, 1000 μ g/ml in 1% HNO₃.
- d) Sodium, B.D.H. Spectrosol, 1000 μ g/ml in 1% HNO₃.

2. pH standards:

- a) Potassium tetroxalate, Hopkin & Williams, Analar.
- b) Potassium hydrogen phthalate, B.D.H., Analar.
- c) Potassium hydrogen tartrate, Hopkin & Williams, Analar.

3. Gases:

- a) Nitrogen, B.O.C., oxygen-free grade.
- b) Hydrogen chloride, B.O.C., technical grade, 99.6% pure.
- c) Nitrous oxide, B.O.C, atomic absorption grade.
- d) Acetylene, B.O.C.

4. Acids:

- a) Sulphuric acid, B.D.H., Analar (specific gravity=1.84).
- b) Hydrochloric acid, Fisons, Analar (specific gravity=1.18).
- c) Nitric acid, Fisons, Analar (specific gravity=1.42).
- d) Perchloric acid, Fisons, Analar (specific gravity=1.70)

e) Orthophosphoric acid, B.D.H., Analar (specific gravity= 1.75).

f) Acetic acid, glacial, B.D.H., Analar.

5. Gas drying agents:

a) Silica gel, self indicating, B.D.H.

b) Calcium chloride, anhydrous, B.D.H., Analar.

6. Vanadium oxides:

a) Vanadium (V) oxide, Fisher Scientific Company, certified 99.9% pure.

b) Vanadium (IV) oxide, Aldrich Chemical Company Ltd, 99.9% pure

7. Chloride analysis:

a) Nitrobenzene, B.D.H., Analar.

b) Silver nitrate, B.D.H., Analar.

c) Ammonium ferric sulphate, B.D.H., Analar.

d) Ammonium thiocyanate, CVS standard concentrated solution capsule.

8. X-ray fluorescence analysis

a) Ethyl cellulose, B.D.H., General purpose reagent grade.

b) Carbon black, B Pearls 1100, Cabot Carbon Ltd.

9. Chlorine analysis:

a) Sodium thiosulphate, Hopkin & Williams, Convol standard concentrated solution capsule.

b) Potassium iodide, B.D.H., Analar.

c) Starch, B.D.H., soluble, Analar.

10. Organics:

a) Dichloromethane, B.D.H., Analar.

b) Trichloromethane, Koc Light laboratories, Analar.

c) Benzene, B.D.H., Analar.

d) Toluene, B.D.H., Analar.

e) Quinoline, B.D.H., general purpose reagent.

f) Dimethylformamide (DMF), B.D.H., Analar.

- g) Dimethyl sulphoxide (DMSO), B.D.H., Analar.
- h) Ethanol, James Burrough, 99.7% min.
- i) Acetone, Hays, general purpose reagent.

11. Others:

- a) Dibutyl phthalate, B.D.H., general purpose reagent.
- b) Iron (III) sulphate, B.D.H., Analar.
- c) Vanadium (IV) sulphate, Aldrich Chemical Company Ltd, general purpose reagent.

2.2 ELEMENTAL ANALYSIS OF THE COKES.

The cokes were analysed by a wet ashing technique; a 3 g sample of coke was carefully weighed and added to a Quickfit 100 ml conical flask which was fitted with a stopper adaptor to increase its height and prevent any loss of material due to spitting or splashing. To the coke 50 ml of concentrated nitric acid were added and the mixture heated in a hot plate to allow the acid to boil gently. Fresh additions of acid were regularly made until all the coke had oxidized. The heating was conducted in a fume cupboard due to the emission of toxic gases and the use of concentrated acids. After the use of considerable quantities of nitric acid a reddish-yellow solution was obtained which was further oxidized by additions of concentrated perchloric acid. This was done by initially adding only a few drops of perchloric acid to the concentrated nitric acid solution and then slowly increasing the perchloric acid concentration by further additions and boiling; thus, the risk of a possible explosion due to contact of perchloric acid with any remaining carbon was avoided. The orange solution obtained was then diluted in 1M nitric acid, made up to 100 ml in a volumetric flask and analysed by atomic absorption spectrophotometry for the metals. Five Flexicoke and two Delayed coke samples were analysed by this technique.

Carbon, hydrogen and sulphur analysis were supplied by Intervep S.A.

2.3 BASIC COKE PREPARATION.

Prior to any leaching or vapour transport experiments the cokes were riffled and divided into 32 equal portions of about 350 g and 390 g for Flexicoke and Delayed coke, respectively. One portion of each coke was sieved to find their particle size distribution. During sieving, 5 minutes shaking time per sieve used was allowed and the mass of coke added to the top sieve was restricted to 50 g.

Grinding was conducted by placing some 40 g of the riffled coke fraction in an agate Tema mill for 5 to 10 minutes, followed by sizing and return of the oversize material to the mill. The whole of a riffled fraction (or several fractions mixed together depending on the quantity of ground coke required) was ground this way. Prior to grinding the cokes were dried for 24 hours at 120°C; this was found to facilitate the sizing operation, by reducing the strong tendency of Flexicoke fines to agglomerate. The oversize material was also dried before regrinding.

Grinding of Flexicoke was difficult and several days were required before a 350 g sample was fully ground and sized. Grinding of Delayed coke was much easier, and no tendency to agglomerate was observed. All ground coke size fractions were checked by laser particle analysis, using a Malvern Instruments 3600 particle size analyser with the coke dispersed in ethanol.

Before any leaching or vapour transport experiment, the coke was dried in an oven at 120°C.

2.4 LEACHING EXPERIMENTS.

The leaching experiments were carried out in a 300ml five necked, glass split reactor. The central neck was occupied by a glass stirrer which passed through a P.T.F.E. stirrer guide to prevent lateral motion of the stirrer. The stirrer was connected to a variable speed motor, the rotation speed of

which was measured by means of a Radio Spares TM-2011 hand held optical tachometer. The other necks contained a thermometer, a sintered glass filter and a double wall water-cooled condenser. The remaining neck was used to introduce the coke into the reactor at the beginning of the leaching reaction. A schematic diagram of the leaching apparatus is shown in Figure 2.1.

The leach liquor in the flask was heated by an electric heating mantle which was connected to a variable transformer to regulate the power input. The transformer was, in turn, connected to a Fi-monitor which controlled the temperature. A control of $\pm 1^{\circ}\text{C}$ could be obtained in the temperature range 50° to 100°C , where a E-Nil thermometer of the range -10° to 110°C with 1°C divisions was used, while a better control of $\pm 0.5^{\circ}\text{C}$ was achieved in the temperature range 20° to 50°C where a Sugden Powell thermometer of the range 0° to 50°C with 0.1°C divisions was used.

The sintered glass filter, of porosity 4, was connected to a 100 ml conical flask, which in turn was connected by a three-way stopcock to vacuum and compressed air lines; at the moment of taking a sample, compressed air was blown through the filter into the leaching vessel to expel any liquid in the glass bulb above the filter and to clean the sintered disk. The vacuum was then connected and a sample of the leach liquor collected in the conical flask. A 5 ml sample was measured with a B grade pipette, and any excess liquid returned to the leaching vessel. Compressed air was then passed through the filter to push back any liquid in the filter stem and bulb and the connecting PVC pipes.

Before the start of an experiment the pH of the leach liquor was measured (at 25°C) by a pH glass electrode connected to a Pye Unicam PTI-15 digital pH meter. A 200 ml volume of the leach liquor was then heated to the required temperature, a 5 g sample of coke added and the clock started. Samples of the leach liquor were regularly collected; these samples were

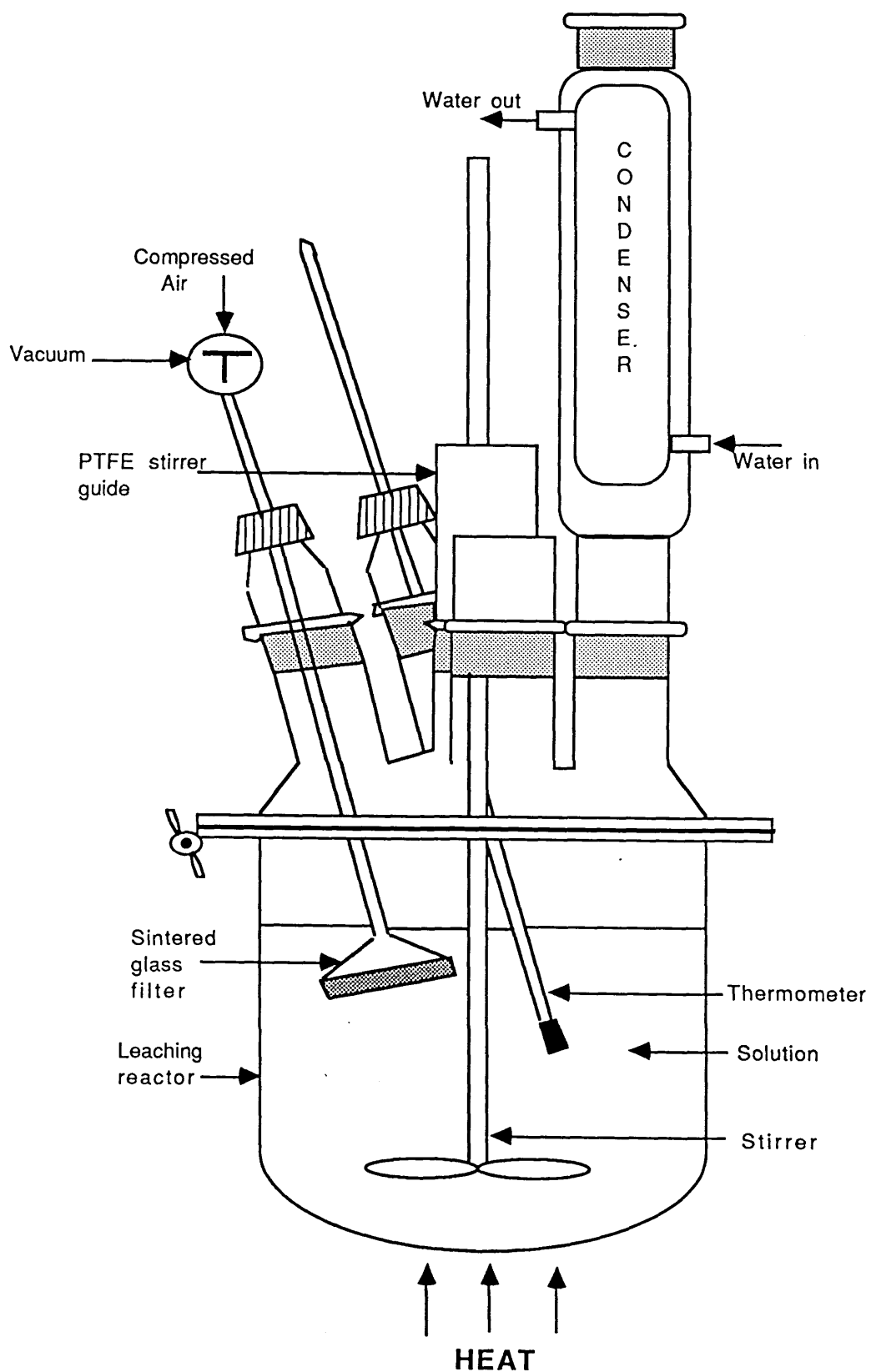


Figure 2.1 Schematic diagram of leaching apparatus.

diluted in the same media as the starting leaching solution and analysed for metal extraction by atomic absorption spectrophotometry. At the end of the experiment the coke was filtered off and the leach liquor cooled and its volume and pH measured.

The pH meter was regularly calibrated with the following standard solutions:

- a) 0.05 M Potassium tetroxalate, pH=1.679 at 25°C.
- b) 0.05 M Potassium hydrogen tartrate, pH=3.557 at 25°C.
- c) 0.05 M Potassium hydrogen phthalate, pH=4.008 at 25°C.

All calibrations were done at 25°C with the standard solution agitated with a small electromagnetic stirrer.

2.5 COKE DISSOLUTION EXPERIMENTS.

A carefully weighed, pre-dried sample of Flexicoke or Delayed coke of about 0.5g, and 60ml of an organic solvent were placed in a Quickfit round bottom flask which was connected to a double walled water-cooled condenser. The organic solvent-coke mixture was then heated by an electric heating mantle to allow gentle boiling of the solvent, which was allowed to reflux for the required period of time. At the end of the experiment the solution was cooled, filtered, its volume measured and a sample taken for atomic absorption and infrared analysis. The reacted coke was dried and weighed. All experiments were conducted in a fume cupboard.

2.6 ATOMIC ABSORPTION SPECTROPHOTOMETRY.

Analysis of the wet ashing solutions, leach liquors and the dissolved products from the vapour transport experiment were analysed by atomic absorption spectrophotometry (AAS) in a Perkin Elmer 2380 atomic absorption spectrophotometer. This is a double beam instrument fitted with background correction and programmable sampling; in all cases it was programmed to take ten, one second measurements per sample, and give the

mean metal concentration and its standard deviation. Three standards in the appropriate concentration range were used to calibrate the instrument; all standards and blank solutions were prepared in the same media as the solution to be analysed. Single element hollow cathode lamps were used. If necessary the samples were diluted in the same media as the solution to be analysed using a Dilutrend automatic diluter.

For vanadium analysis an N₂O-acetylene flame was used, whilst for nickel, iron and sodium an air-acetylene flame was used. The experimental conditions for each metal analysed and the linear range of standards in aqueous solutions, are given in Table 2.1.

Element	Wavelength nm	Slit width nm	Linear range,ppm	Sensitivity at 1% absorption,ppm
Vanadium	318.4	0.7	Up to 150 ppm in aqueous solutions	1.70
Nickel	232.0	0.2	Up to 5 ppm in aqueous solutions	0.15
Iron	248.3	0.2	Up to 5 ppm in aqueous solutions	0.12
Sodium	589.6	0.7	Up to 1 ppm in aqueous solutions	0.015

Table 2.1 Experimental conditions for the atomic absorption spectrophotometer.

Organic solutions were analysed with an IL-455 flameless atomic absorption spectrophotometer. A 20μl volume of the organic sample was injected into a graphite cuvette. All analyses were conducted with background correction and in

peak area mode. The metal standards used were prepared in aqueous solutions. When dilutions were required ethanol was used. Single element hollow cathode lamps were used; the wavelength settings are given in Table 2.1.

2.7 THERMOGRAVIMETRIC ANALYSIS.

A Stanton Redcroft STA-780 instrument was used for thermogravimetric analysis of Flexicoke and the products obtained from the vapour transport experiments. The balance had an accuracy of 10^{-5} g, and could support a maximum temperature of 1500°C. A platinum crucible was used for all work; the inert reference material, also in a platinum crucible, was α -alumina, whose weight was matched to the initial sample weight at the beginning of each run. The instrument controlled heating and cooling rates, maximum and minimum temperatures and dwell temperature and time. Plots of thermogravimetry, TG (mass versus temperature or time), differential thermal analysis, DTA (dT/dt versus temperature or time) and derivative thermogravimetry, DTG (dM/dt versus temperature or time) could be obtained. The experimental conditions are given with each plot in Chapter 5.

2.8 VAPOUR TRANSPORT EXPERIMENTS.

The vapour transport experiments were conducted in two types of experimental reactor, one with a fixed bed of coke (Apparatus A, shown in Figure 2.2) and other with a fluidized bed (Apparatus B, shown in Figure 2.3). The experiments were performed using factorial design techniques, plus a number of other runs to complement the designs. Factorial designs 1 and 2 were conducted in apparatus A and factorial design 3 in apparatus B. Nothing will be said about factorial designs as an experimental technique: their construction, analysis and benefits are presented in a number of excellent text books [122, 125, 126], and their use has been extensively reviewed and demonstrated by past students of the Hydrometallurgy Group [138].

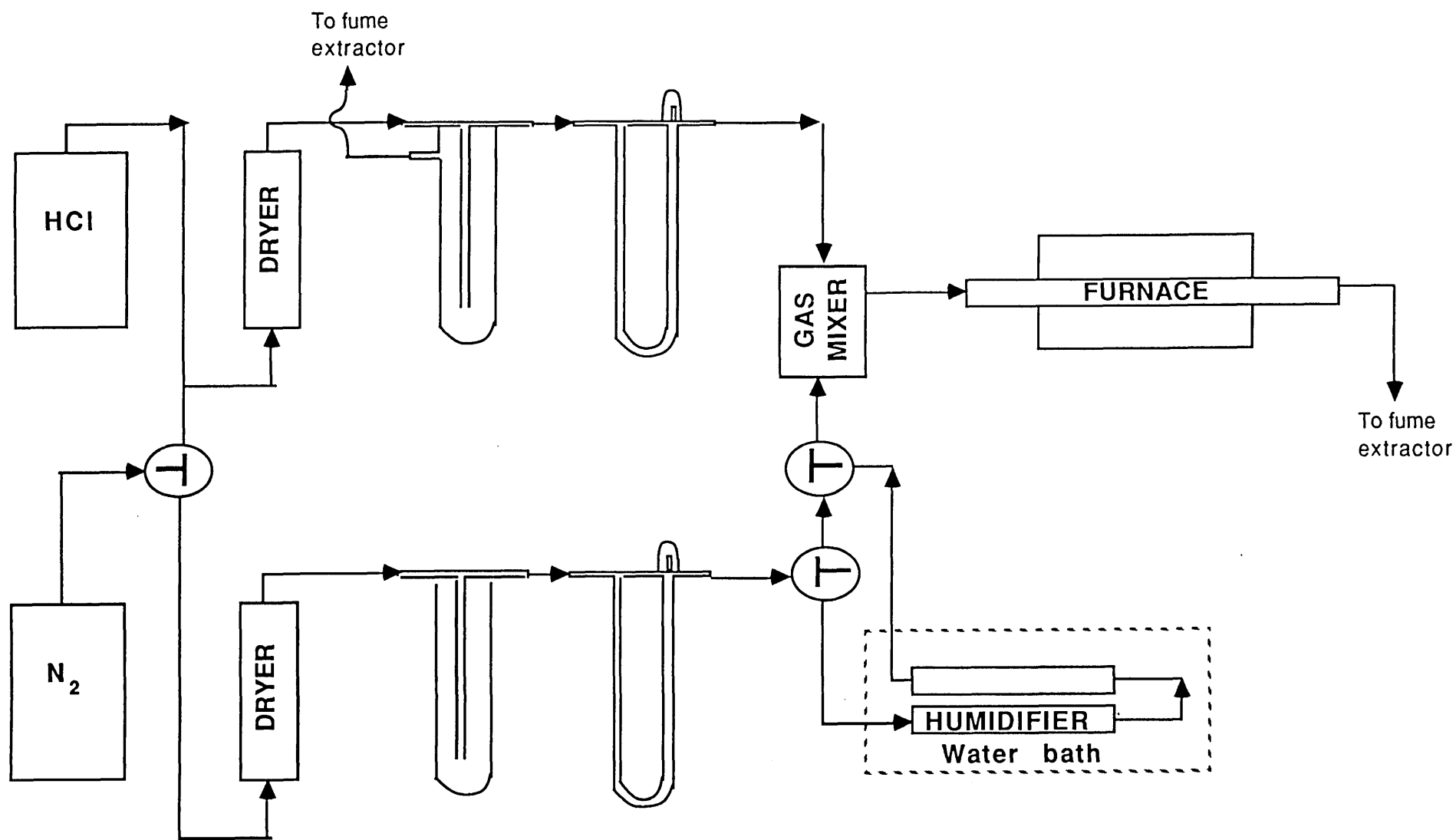


Figure 2.2 Schematic diagram of fixed bed apparatus and gas train.

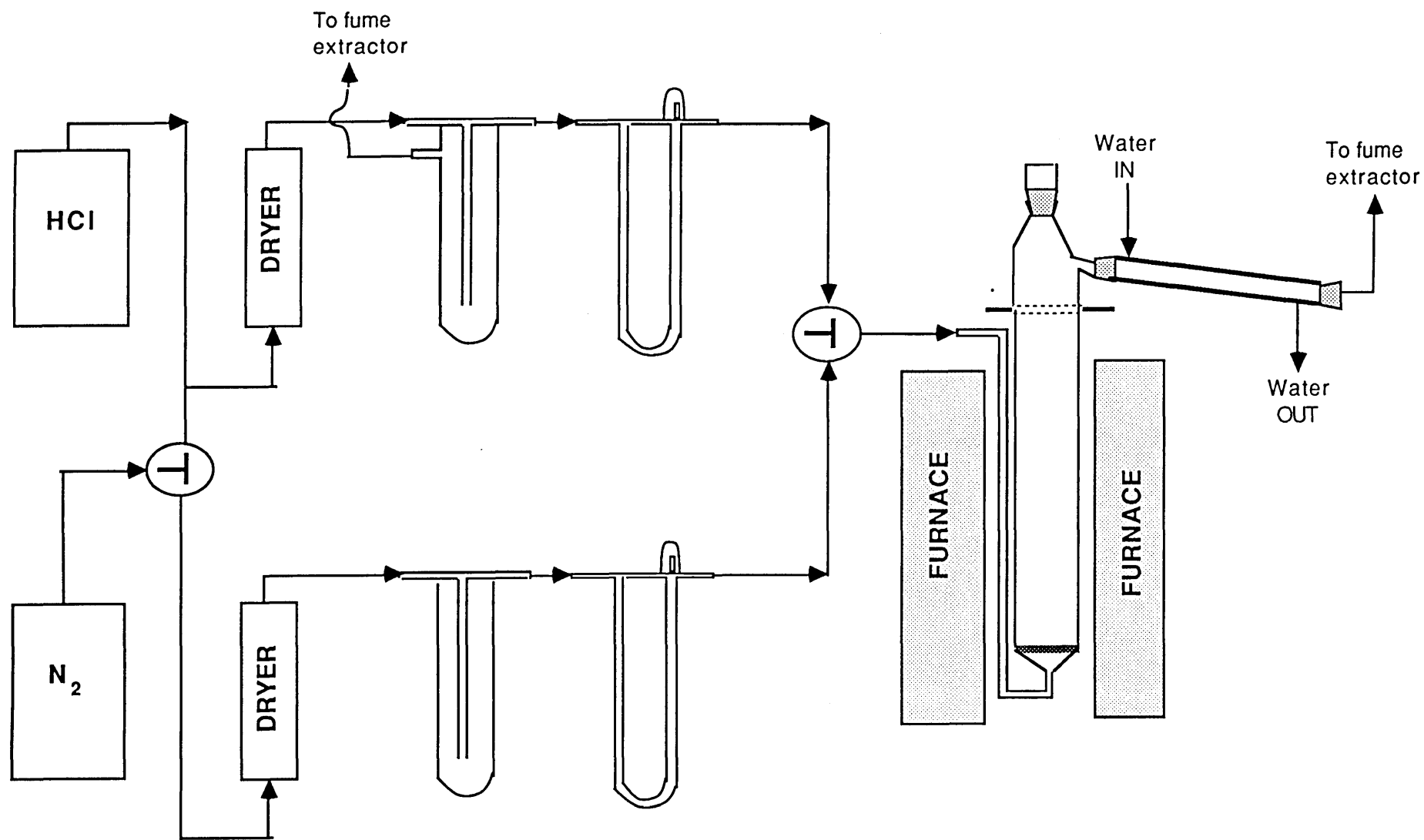


Figure 2.3 Schematic diagram for fluidized bed furnace and gas train.

The gas flow rates and HCl partial pressure in both apparatus A and B were controlled by means of capillary gas flow meters. Oxygen-free-nitrogen and hydrogen chloride gas, from gas cylinders, were dried by flowing through a column filled with a drying agent (anhydrous calcium chloride for HCl and self-indicating silica gel for N₂). The constant height bubblers (adjusting the height of which allowed for changes in flow rate) and manometers were filled with dibutyl phthalate for the nitrogen side and concentrated sulphuric acid for the HCl side. Before heating the coke, the HCl partial pressure was set, using only nitrogen, by measuring the flow rates of nitrogen and combined gases. Flow rates were measured by the rising soap bubble technique; the flow meter was placed at the exit of the reactor, so as to take into account the pressure drop across the coke bed. No correction was made for the density and viscosity of HCl when measuring flow rates.

Apparatus A employed a long silica tube (o.d.=1.46 cm) into which a weighed amount of coke was placed between two plugs of silica wool. The tube was placed in a horizontal furnace (length=40 cm, i.d.=4.5 cm), with the coke bed lying in the hot zone of the furnace. The temperature profiles of the furnace when set at 800° and 1000°C, with a gas flow rate of 4.5 ml/sec (at 20°C) are given in Figure 2.4; a hot zone of approximately 10 cm length was obtained. The coke was heated to the required temperature under a flowing nitrogen atmosphere and the experiment started by allowing the N₂-HCl gas mixture to flow into the reactor. For factorial design 1 the gases mixed and entered the reactor; for factorial design 2 the nitrogen stream flowed first through a humidifier and then mixed with the HCl gas. The humidifier, which controlled the partial pressure of water vapour, consisted of two columns filled with a 9 to 1 mixture of hydrated and anhydrous oxalic acid [139]. The mixture was maintained in a constant temperature water bath, which allowed different levels of humidity to be set according to the bath temperature. The exit gases from the reactor were cooled by an external water-

cooled condenser (made from lead pipe), bubbled through a solution of sodium hydroxide (to absorb and neutralize the HCl gas) and disposed through the soap bubble meter to fume extraction. At the end of each run the coke was collected by removal from the gas entry side; the vapour transport products were then collected, dissolved in 1M sulphuric acid and analysed for vanadium, nickel and iron by atomic absorption spectrophotometry. The NaOH scrubber solution was also analysed by atomic absorption spectrophotometry.

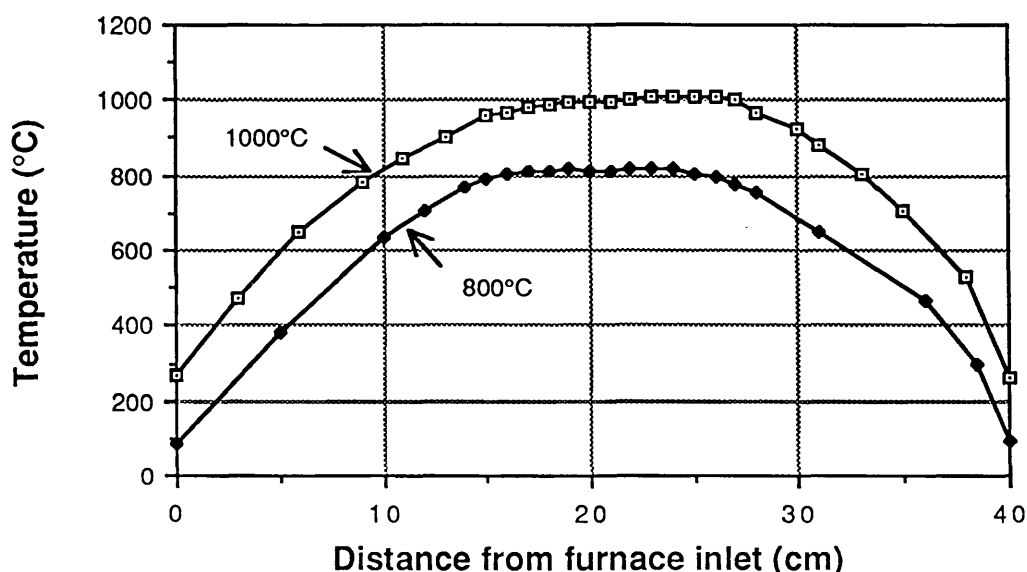


Figure 2.4 Temperature profile in the horizontal tube furnace at a set temperature of 800° and 1000°C, with a flow rate of 4.5 ml/sec (at 20°C).

Apparatus B consisted of a fluidized bed reactor (i.d.=3.1 cm, length=41 cm) made from silica tubing with a sintered silica disk (pore size 40 to 100 μ m, porosity 2) as distributor. The reactor was connected, by means of a ground silica flange, to a borosilicate glass lid with two necks, one which allowed an alumina sampling spoon to be introduced into the fluidized bed, and the other which led the exit gases through a water cooled condenser to fume extraction.

The reactor was heated in a vertical, two-zone, tube furnace (i.d.=5.1 cm, length=55 cm). The temperature profile inside the reactor tube, with a gas flow rate of 4.2 ml/sec (at 20°C), and a fluidized coke bed of 6-7 cm, is given in Figure 2.5; as can be seen the temperature in the coke bed was constant up to a height of 12 cm from the distributor. At a height of 20 cm from the distributor there was only a 25°C drop in temperature, reflecting the advantage of a long hot zone obtained from using a two-zone furnace. The bottom of the furnace was sealed with kaolite wool to reduce heat loss and drafts of cold air. The gas mixture was preheated before entering the reactor by flowing through a silica tube (i.d.= 0.7 cm) which lay parallel to the reactor and which was connected at the bottom to the gas distributor.

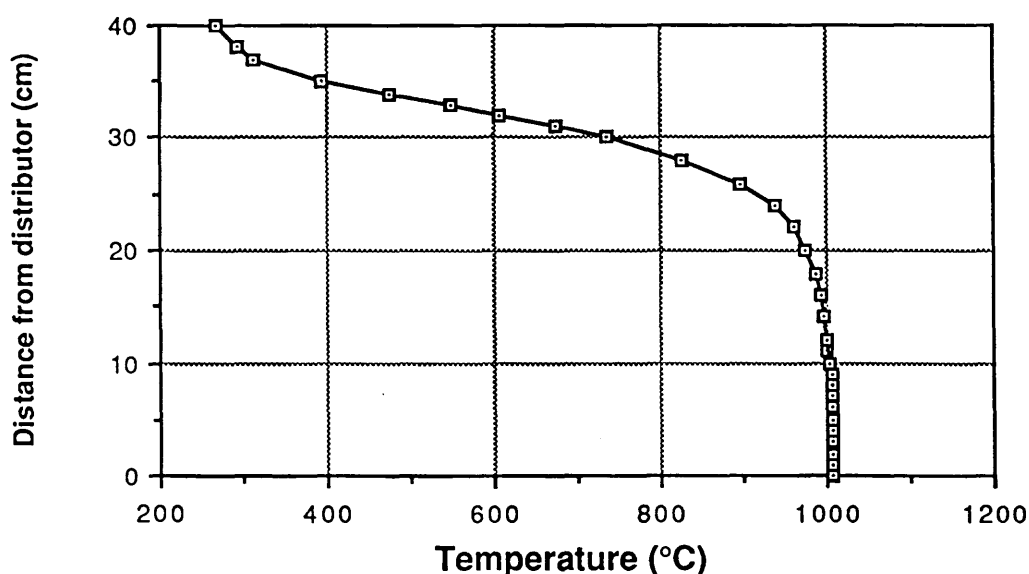


Figure 2.5 Temperature profile in the fluidized bed reactor at a set temperature of 1000°C with a gas flow rate of 4.2 ml/sec (at 20°C).

The sampling alumina spoon was made from an alumina crucible (i.d.=1 cm, length=2 cm) and an alumina thermocouple rod (o.d.=0.2 cm, length=60 cm); they were joined by the use of

alumina cement prepared with 50% orthophosphoric acid solution allowed to dry and fired at 1000°C for 2 hours.

The reactor, with the coke, was introduced into the hot furnace and allowed to preheat for 30 minutes under a nitrogen atmosphere; with ground coke the reactor was introduced into the cold furnace and slowly heated (to maintain the gas flow rate low and thus reduce the degree of coke elutriation). A coke sample was collected and the experiment started by passing the HCl-N₂ gas mixture; coke samples were taken at regular times and analysed by x-ray fluorescence spectrometry (XRF) for residual metal content. At the end of an experiment the solid products were collected, dissolved in 1M nitric acid and the solution analysed for vanadium, nickel, iron and sodium by atomic absorption spectrophotometry and for chloride by titration using Volhard's method.

5.9 X-RAY FLUORESCENCE SPECTROMETRY.

X-ray fluorescence spectrometry (XRF) was used to analyse for residual vanadium and nickel in the coke samples obtained from the vapour transport experiments. A Link System XRF-500 instrument was used; analysis were conducted in the energy dispersive spectrophotometry mode with a silver filament; the voltage was set at 15 kV, with 100 seconds counting time and the current adjusted to give a dead time of 40%. Samples for analysis were prepared by mixing approximately 1g of coke with an equal quantity of ethyl cellulose, shaking the mixture with two glass balls in an orbital shaker, and pressing the mixed powder into a disk shape pellet (2.5 cm diameter). The instrument corrected for atomic number, absorption and background fluorescence effects.

Eight standards for calibration were prepared; these were made by adding small and carefully measured quantities of vanadium and nickel solutions to hot carbon black. Carbon black was chosen because of its purity; it was heated to quickly evaporate the solution leaving the metal behind. Adding the metal in the

form of a solution is the preferred method for XRF standard preparation for low metal concentrations, since a better distribution of the metal can be achieved. The loaded carbon black was thoroughly shaken, divided into eight equal portions with a spinning riffler, and diluted to the required concentration with fresh carbon black. The loaded-fresh carbon mixture was then mixed with an equal weight of ethyl cellulose, shaken and pelletised.

2.10 ELECTRON MICROSCOPY WORK.

Initial observations were made with a Jeol 35-CF scanning electron microscope. The microscope was fitted with a microprobe, with which energy dispersive (EDS) and wave dispersive spectrophotometric (WDS) analysis can be made. The facilities available were not sufficiently precise to measure the very low levels of metal found in the cokes. Further work was conducted on a Camebax-Micro scanning electron microscope. This instrument was fitted with four spectrophotometers which allowed simultaneous analysis of four elements. All analysis were conducted in the WDS mode, with an acceleration voltage of 15 kV, and a current of 40×10^{-9} Amps.

The vanadium, nickel and sulphur analysis of coke particles as a function of the radial distance, shown in Chapter 5, were obtained by programming the microprobe to analyse for these elements every $2\mu\text{m}$ along a given particle diameter. The analysis was performed by measuring the x-ray counts for 30 seconds, at every position, at the K band peak; the spectrophotometer then automatically moved $50\text{\AA}$ to each side of the peak and measured the background readings for 15 seconds on each side. The long counting times were required because of the low metal concentrations. Corrections for atomic number, absorption and background effects were made by the programme.

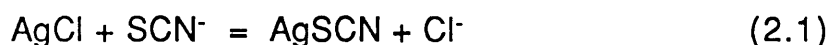
2.11 X-RAY DIFFRACTION.

The x-ray diffraction (XRD) work was conducted in a Phillips 1710 spectrophotometer, using Cu K α radiation; the instrument was set at 40 kV and 40 mA.

2.12 CHLORIDE ANALYSIS.

The chloride concentration of solutions, obtained from dissolving the products from the vapour transport experiments in 1M nitric acid, was found by Volhard's method. In this method the chloride is precipitated with an excess of 0.10 M silver nitrate solution, and the excess determined by titration with thiocyanate ion, using ferric ion as the indicator. Standard solutions of 0.10 M silver nitrate and 0.050M ammonium thiocyanate were used. The indicator was prepared by making a saturated solution of ammonium ferric nitrate, filtering and acidifying with a small quantity of 6M HNO₃; it was used as soon as possible and kept in iced water.

The chloride in a 10 ml aliquot of the unknown solution, in a 250 ml conical flask, was precipitated with excess silver; to this solution a few ml of nitrobenzene were added to coat the AgCl precipitate and avoid reaction 2.1:



AgSCN is more soluble than AgCl and hence chloride would be released on adding thiocyanate; this was avoided with the addition of nitrobenzene. The solutions were always vigorously shaken (otherwise AgCl absorbs Ag⁺). 1 ml of the indicator was added and the titration with SCN⁻ started. The end point is reached when the colour of the solution changes from white to a light brown; just before the end point the solid coagulates. The end point was checked by further additions of Ag⁺ followed by SCN⁻ titration.

2.13 CHLORINE ANALYSIS.

Chlorine was analysed by reaction with iodide, which is oxidized to iodine and analysed by the classic thiosulphate-starch titration. The determination of Cl_2 from the exit gases of the fluidized bed reactor in the vapour transport experiments is, however, not straightforward because H_2S is also liberated and this reduces iodine back to iodide. To avoid, or at least reduce this complication, the coke was heated under nitrogen for 3 hours at 1000°C , rather than the customary 30 minutes; in this way the H_2S gas was driven out. At the end of this period the gases were bubbled into a solution of 0.1 M potassium iodide and the experiment started. The bubbler was placed far from the reactor, to allow sufficient time for the metal chlorides to condense and avoid any redox reactions between vanadium and iodide or iodine; the potassium iodide solution was kept in ice water to improve the absorption of chlorine and reduce the decomposition of iodide to iodine. After 3 hours of reaction, aliquots of the iodide solution were titrated with standard 0.1 M sodium thiosulphate using a 1% starch solution as indicator.

2.14 SPECIFIC SURFACE AREA MEASUREMENTS.

The specific surface area of the cokes was measured with a Quantachrome Monosorb MS-4 instrument; the equipment was calibrated by injecting a known volume of air. A carefully weighed sample of coke, held in a U-shape sample holder, was then immersed in liquid nitrogen while a gas mixture of 30% nitrogen and 70% helium flowed through the coke. Nitrogen was absorbed by the coke; the sample was then quickly immersed in water, and the quantity of nitrogen desorbed measured. The instrument automatically gave the surface area of the coke sample, which was divided by the mass of the coke to give the specific surface area. Each sample was analysed three times.

2.15 SOLUBILITY EXPERIMENTS.

The solubility of vanadium (V) oxide and vanadium (IV) sulphate in sulphuric acid was investigated by dissolving the pure oxide or sulphate in sulphuric acid solutions of various concentrations. The powder and acid mixture, in a 250 ml conical flask, was placed in constant temperature shaker and left till the powder dissolved. More oxide or sulphate was added every few days until no more dissolution took place. The saturated solutions were then filtered (using glass fibre filter paper) and analysed by atomic absorption spectrophotometry.

2.16 GAS CHROMATOGRAPHY.

Samples of the exit gas stream from the vapour transport experiment were collected in glass bubbles; these had a plastic tap at each end which allowed the gas to flow through the bubble and contain it when sealed. The gas in the bubbles was then pressurized to about 1.5 bar with oxygen-free-nitrogen, and injected into a Pye Unicam GDC gas chromatograph. The gas chromatograph was fitted with a flame ionization detector; the column used was a pore packed QS column (length=2m, i.d.=0.2cm), and the analyses were conducted under standard temperature (25° to 180°C, with a heating rate of 8°C/min) and standard gas flow rate (30ml/min). Nitrogen was used as the carrier gas.

3. PROPERTIES OF THE COKES.

Table 3.1 below gives the chemical analysis for Flexicoke and Delayed coke. As can be seen from this table the metal content of Flexicoke is much greater than in Delayed coke; the vanadium to nickel ratio is about the same for both cokes (5.2-5.7), but there is far more iron in Delayed coke than in Flexicoke. The sulphur content of Delayed coke is also greater. At 1200°C the volatile content of the cokes (from TG/DTA/DTG analysis in nitrogen) was found to be 7.64 wt% and 13.26 wt% for Flexicoke and Delayed coke, respectively.

Element	Flexicoke	Delayed coke
Carbon, wt%	91.82	90.32
Hydrogen, wt%	1.40	3.38
Sulphur, wt%	2.53	3.35
Nitrogen, wt%	-	1.46
Oxygen, wt%	-	1.49
Vanadium, ppm	10200	1710
Nickel, ppm	1970	300
Iron, ppm	174	440
Sodium, ppm	490	250

Table 3.1 Elemental composition of Flexicoke and Delayed coke.

Figure 3.1 and 3.2 give the particle size distribution for as-received Flexicoke and Delayed coke, respectively. The average particle size for Flexicoke was found to be about 143 μ m, whilst for Delayed coke it was 156 μ m. The particle size distribution for Delayed coke has a wide spread, while Flexicoke shows a reasonably symmetrical normal distribution, with almost 50% of the coke found in the 150+125 μ m size

fraction. The Flexicoke particle with diameters greater than 212 μ m were agglomerates of smaller Flexicoke particles; agglomerates as large as 10mm were found.

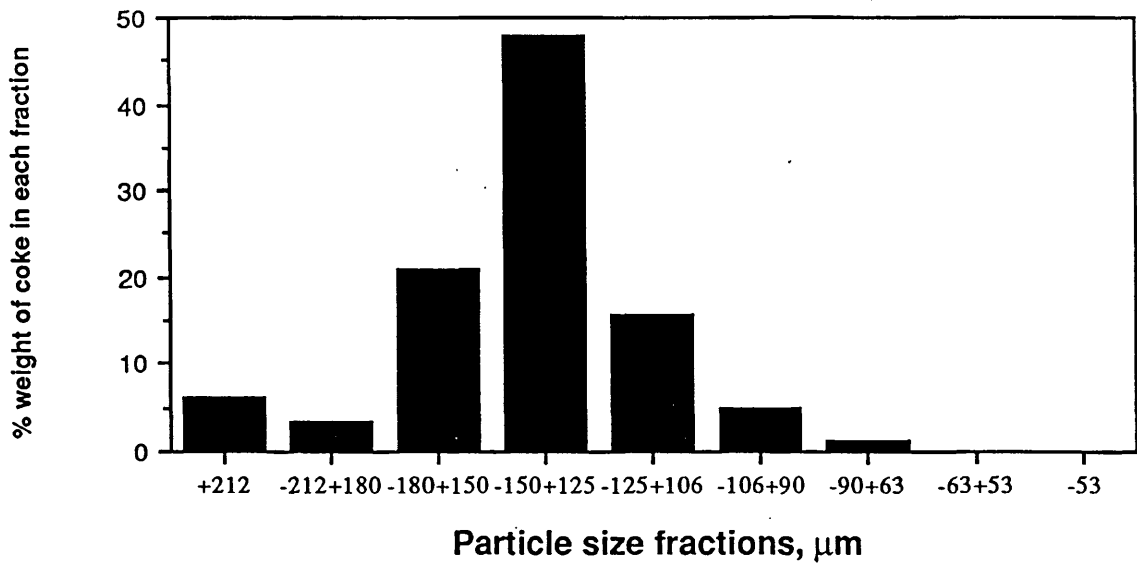


Figure 3.1 Size distribution of as-received Flexicoke particles.

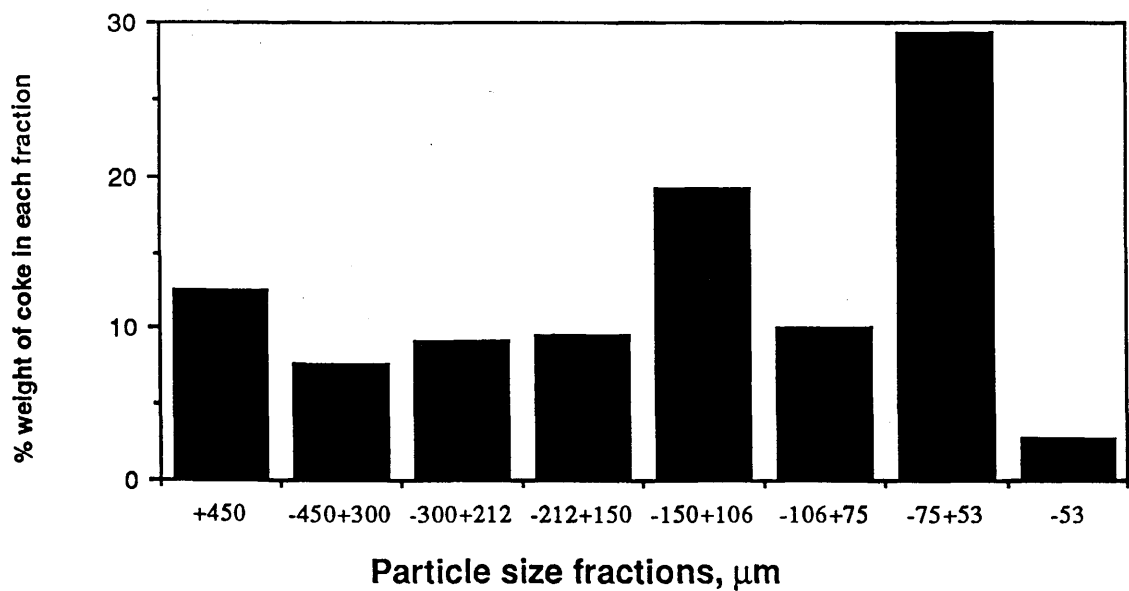


Figure 3.2 Size distribution of as-received Delayed coke particles.

Plates 3.1 and 3.2 show typical cross-sections of Flexicoke and Delayed coke particles under the same magnification. The Flexicoke particle is seen to be roughly spherical and to have an "onion skin" appearance from the repeated deposition of thin layers of coke on the seed particle. The Delayed coke particle shows little sphericity (as expected from the mechanical crushing which it received on removal from the coke drums), and are smooth and of uniform microstructure.

Plate 3.3 shows a scanning electron micrograph of the cross-section of a Flexicoke particle, and Plates 3.4, 3.5 and 3.6 show the concentration distribution of vanadium, nickel and sulphur, respectively, for the particle shown in Plate 3.3. It may be seen that both vanadium and nickel seem to be concentrated in a ring outside the seed particle, while sulphur is concentrated in the deposited coke layers. Thus, the two metals of interest are concentrated in a thin spherical shell in the particle interior and hence solid state diffusion might be expected to be the rate controlling step in the extraction of these metals. Further work on the microprobe revealed that iron is found in very small concentrated pockets on the exterior of the particle, although as shown in Plate 3.7 iron can also be found in the centre of the particle (a grain of pyrite is shown to act as the seed particle).

Quantitative analysis of the coke particle, using WDS microprobe, has revealed that the nickel shell is outside the vanadium shell, and that nickel is associated with sulphur, whereas vanadium shows no association with sulphur. Plates 3.8 and 3.9 show how where the nickel concentration peaks, the sulphur concentration also peaks. Iron is also likely to be associated with sulphur, as revealed by the pyrite particle shown in Plate 3.7. Small particles rich in calcium and sulphur have also been detected. The remaining sulphur is associated with the carbon phase. Under the highly reducing conditions and high temperatures found in the gasifier of the Flexicoking

process, nickel sulphide would not be reduced by carbon monoxide, and all the vanadium oxides are thermodynamically more stable than CO below 900°C. Thus, nickel is probably in the form of nickel sulphide, vanadium as vanadium oxide (probably V_2O_4) and iron as iron sulphide. The sodium is the cokes probably exists as NaCl (some chlorine has been detected by x-ray fluorescence analysis).

Vanadium, nickel and iron were found to be uniformly distributed in Delayed coke.

Table 3.2 below gives some physical properties of Flexicoke and Delayed coke.

Property	Flexicoke	Delayed coke
Mean particle size, μm	143	156
Standard deviation, μm	28	131
Coke density , Kg/m^3	1440	1250
Bulk density, Kg/m^3	880	935
Specific surface area, m^2/g	2.53	0.73
pH of Zero potential	0-0.5	-
Moisture content, wt%	0.10	0.60

Table 3.2 Some physical properties of Flexicoke and Delayed coke.

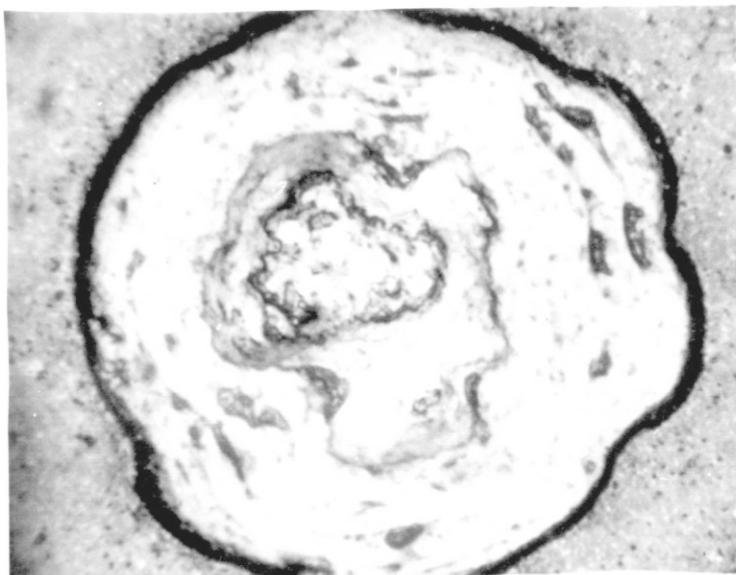


Plate 3.1 Optical microscope image of the cross-section of a Flexicoke particle; magnification= 320x.

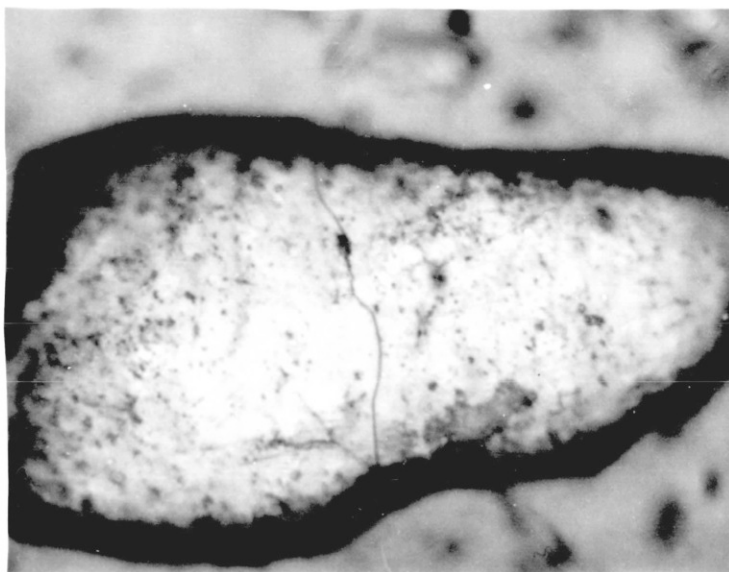


Plate 3.2 Optical microscope image of the cross-section of a Delayed coke particle; magnification= 320x.

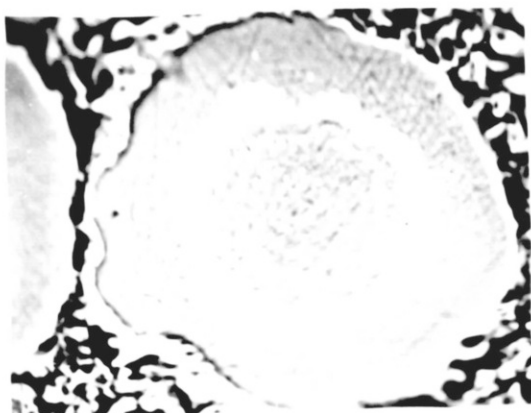


Plate 3.3 SEM of cross section of cross-section of Flexicoke particle, magnification=600x.

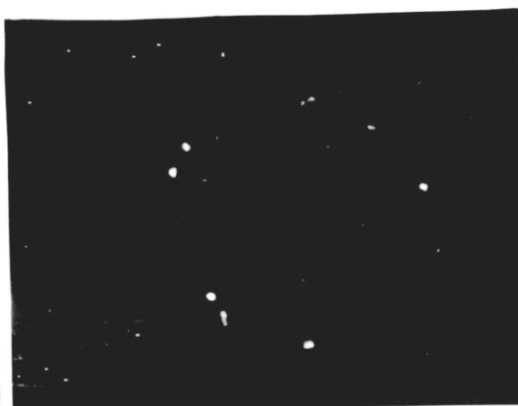


Plate 3.4 Vanadium distribution of cross-section of Flexicoke particle, magnification=600x.

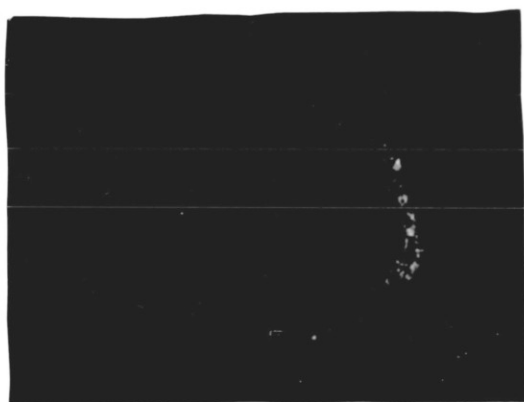


Plate 3.5 Nickel distribution of cross-section of Flexicoke particle, magnification=600x.

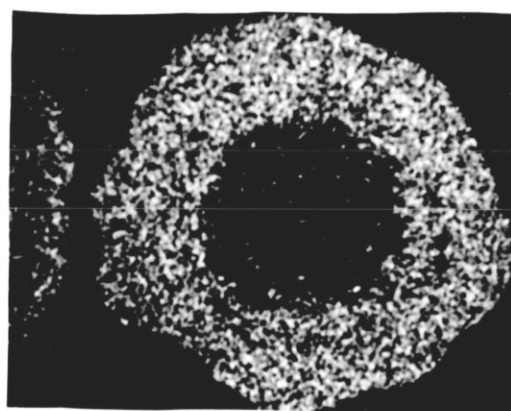


Plate 3.6 Sulphur distribution of cross-section of Flexicoke particle, magnification=600x.

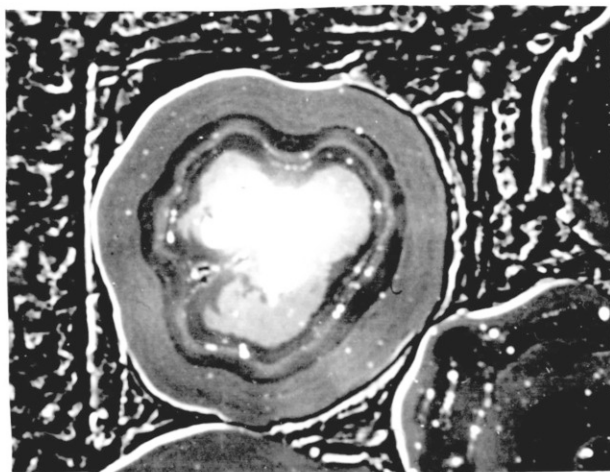


Plate 3.7 SEM of cross section of Flexicoke particle with pyrite particle as nucleus; magnification=600x.

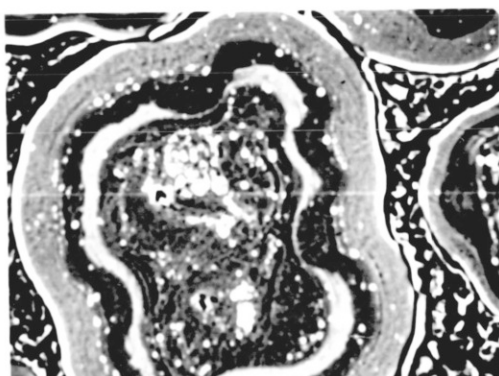


Plate 3.8 SEM of cross-section as-received Flexicoke particle magnification=600x.

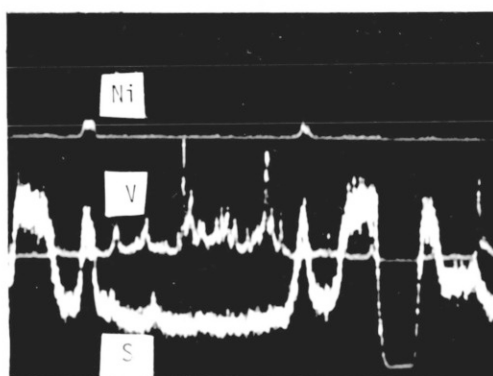


Plate 3.9 Line analysis of Ni, V and S distributions in a Flexicoke particle, Mg=600x.

4. HYDROMETALLURGY EXPERIMENTS.

RESULTS AND DISCUSSION.

4.1 LEACHING OF AS-RECEIVED FLEXICOKE.

Table 4.1 shows the results obtained from leaching the as-received Flexicoke with various aqueous reactants at different temperatures and leaching times. From this table it may be seen that water extracts about half the vanadium and nickel extracted by 1M sulphuric acid at the same temperature. The results given in Table 4.1 show disappointingly low levels of extraction for both nickel and vanadium. Changes in leaching temperature had little effect on the vanadium yield, as shown in Figure 4.1; increases in acid concentration produced a moderate increase in the vanadium extraction. The addition of oxidizing reagents, such as Fe^{3+} , appeared to increase the initial vanadium extraction, but as shown in Figure 4.2 the maximum extraction obtained is independent of the leachant used.

Leachant	Temperature (°C)	Time (min)	% Vanadium extraction	% Nickel extraction
Distilled water	80	150	3.4±0.4	0.6±0.4
1M H_2SO_4	40	120	5.9±0.8	-
1M H_2SO_4	60	120	5.8±0.8	0.4±1.0
1M H_2SO_4	80	120	7.5±0.8	1.2±1.2
2M H_2SO_4	80	120	10.6±0.5	5.5±5.0
1M NaOH	80	300	9.3±0.9	-
0.1M Fe^{3+} in 2M HCl	80	1140	12.4±0.8	12.4±6.0
2M HCl	80	1020	4.3±1.3	1.9±0.4

Table 4.1 Vanadium and nickel extractions obtained from the aqueous leaching of as-received Flexicoke.

The extraction of nickel was also low, in many cases approaching the limits of detection of the atomic absorption spectrophotometer (hence the large standard deviations obtained). Increases in acid concentration and additions of oxidizing reagents increased the nickel recovery; increases in leaching temperature may have increased the nickel extraction, but with such high analysis error no definite conclusions can be made. In general, nickel was very unresponsive to aqueous leaching, and in most cases only trace amounts were found in solution.

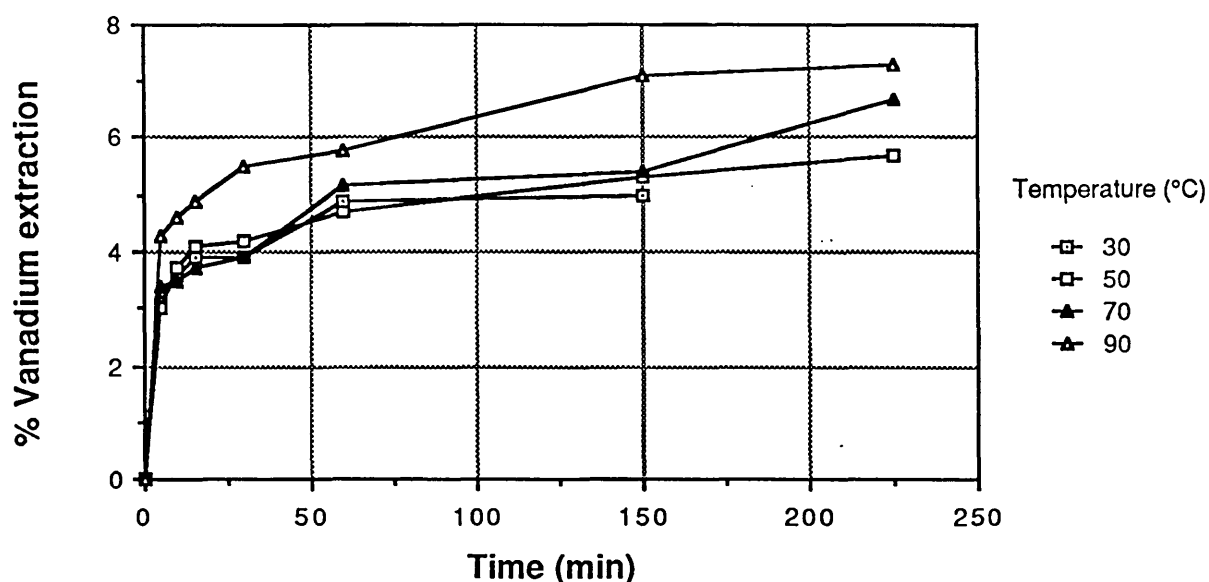


Figure 4.1 Effect of leachant temperature on the vanadium extraction from as-received Flexicoke; 1 M H_2SO_4 , 550 rpm agitation speed.

The use of organic solvents for metal extraction from Flexicoke was also investigated. Table 4.2 gives the vanadium extraction obtained from leaching the as-received Flexicoke at the boiling point of the solvent, under refluxing conditions, for the given leaching times. The table also gives the percentage coke dissolution obtained during leaching. A negative degree of dissolution indicates an increase in coke mass. This parameter gives an indication of the interaction between the coke and the

solvent. For example, Flexicoke and quinoline interact to such an extent as to produce a 35% increase in coke mass, which is associated with a large increase in coke volume (around 300%) and the formation of a tar-like residue. As can be seen from Table 4.2, the coke-solvent interaction does not necessarily increase the vanadium extraction from Flexicoke.

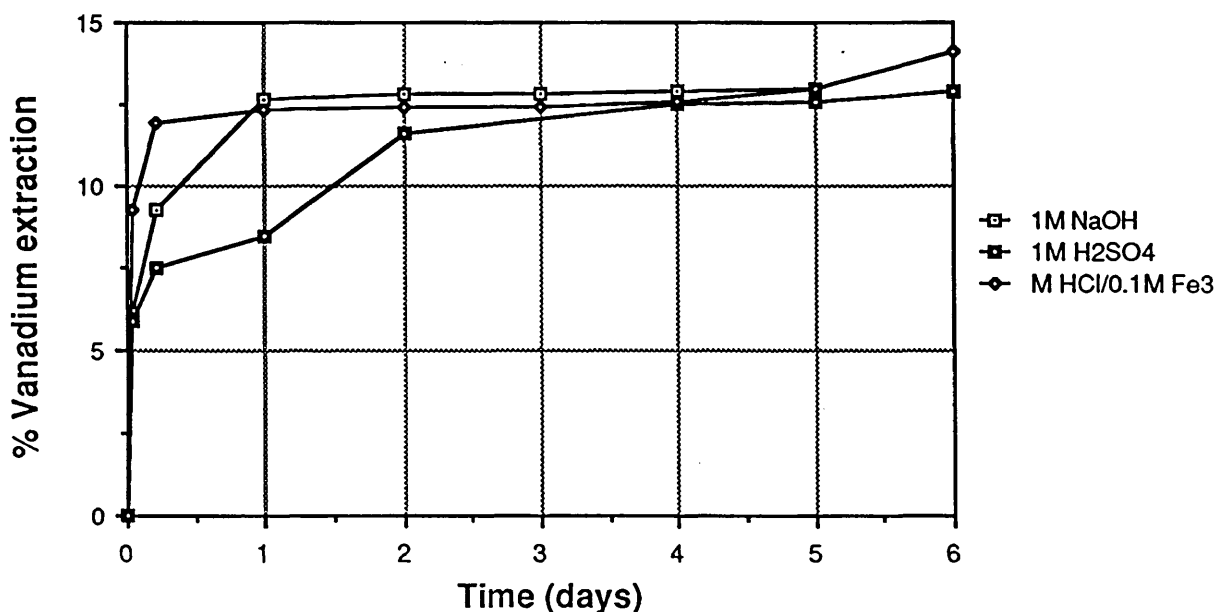


Figure 4.2 Effect of various leachants on the vanadium extraction from as-received Flexicoke; 80°C, 550 rpm agitation speed.

Table 4.2 shows that purely aromatic solvents, such as benzene, are not effective in extracting vanadium from Flexicoke. Addition of polar groups, such as additions of ethanol to benzene, appear to increase the metal extraction. However, no obvious correlation between solvent polarity and metal extraction can be identified, since DMF and DMSO give lower yields than less polar solvents. Increases in reaction time also appeared to have little influence on the vanadium extraction and on the change in coke mass. Furthermore, the vanadium extractions are in all cases lower than those obtained with aqueous leachants. Nickel extraction was negligible in all cases.

Solvent	% Coke dissolution	Time (hours)	% Vanadium extraction	Observations
Dichloromethane	-2.4	24	0.06	Clear solution
DMF	1.2	8	0.12	Clear solution
DMF	1.2	96	0.50	Clear solution
Toluene	4.8	8	0.12	Clear solution
Toluene	5.1	96	0.12	Clear solution
Chloroform	2.7	8	0.35	Clear solution
Acetic acid	-0.8	8	0.71	Clear solution
DMSO	2.9	8	1.06	Amber solution
DMSO	3.1	96	2.12	Amber solution
Quinoline	-34.8	144	0.02	Tar like residue
Benzene	14.7	144	0.02	Clear solution
2 Benzene:1 Ethanol	-1.7	120	3.42	Clear solution
1 Benzene:2 Ethanol	6.8	144	4.24	Clear solution

Table 4.2 Vanadium extraction and coke dissolution by organic solvents from as-received Flexicoke; as-received Flexicoke, dissolution conducted at the boiling point of the solvent.

Some of the extracts obtained from the reaction of the organic solvent with Flexicoke were analysed by infrared spectrophotometry and the results are given in Table 4.4 (at the end of the Chapter).

Measurements of the specific surface area of as-received Flexicoke by nitrogen chemisorption gave a surface area of only 2.53 m²/g; mercury porosity measurements indicate that (in the range of between 30 to 300,000Å pore radius) there is very little porosity present in the coke. This low porosity and surface area, combined with the lower concentration of vanadium and nickel at the particle surface (compared to the interior) and the low metal extractions obtained, indicates that little diffusion of the aqueous reactant into the Flexicoke

particle takes place. Even with the organic reactants, where in some cases there is considerable disruption of the intermolecular and hydrogen bonding of the coke, there is no increase in the metal recovery. The fact that the reaction kinetics are controlled by diffusion is reflected by the very low increases in metal extraction with increases in leaching temperature, as shown in Table 4.1 and Figure 4.1.

4.2 LEACHING OF GROUND FLEXICOKE.

The low vanadium and nickel yields obtained from the leaching of as-received Flexicoke led to an investigation of the behaviour of ground coke. Grinding the Flexicoke was generally difficult; a sample of about 350 g of Flexicoke required several days grinding in a Tema mill before the required size fraction was obtained. Grinding was conducted in an agate mill for short periods of time (5-10 min), followed by sizing and return of the oversize material to the mill for regrinding. In this way excessive production of fines was avoided. The coke fines had a strong tendency to agglomerate, making the sizing operation difficult; this problem was largely eliminated by drying the as-received and oversize coke at 120°C before grinding or regrinding. Wet sieving of the Flexicoke was not possible as a large portion of the vanadium was water leachable. The sized fractions obtained from the sieving operation were checked by the use of a laser particle size analyser. Bond [112] reports the work index for grinding of petroleum coke to be 73.8, a very high value, only surpassed by mica.

4.2.1 Effect of temperature.

Vanadium extraction versus time curves for ground Flexicoke at different leaching temperatures are given in Figure 4.3 below. 1M sulphuric acid, -53 μ m coke and a stirring speed of 550 rpm were used throughout. Nickel extractions were low and varied between 2.6% at 30°C to 17.4% at 80°C after 180 minutes. In all cases the filtered leach liquor showed a deep blue colour

characteristic of the oxovanadium (IV) ion, VO^{2+} . Some of the Flexicoke floated on the leachant surface, indicating a small degree of non-wettability. This was solved by the addition of a surfactant, such as a dilute liquid detergent solution; however, as no improvement in metal extraction was obtained the use of the surfactant was discontinued. Coke was also found to "creep-up" the container walls; no solution to this problem was found. On adding the coke to the acid leachant a strong smell of H_2S was detected. The vanadium extractions obtained were good, particularly at the higher leaching temperatures. The extraction curves shown in Figure 4.3 are average readings of two experiments. Considerable scatter was obtained between individual runs, with errors of up to $\pm 10\%$ in the final extraction being found.

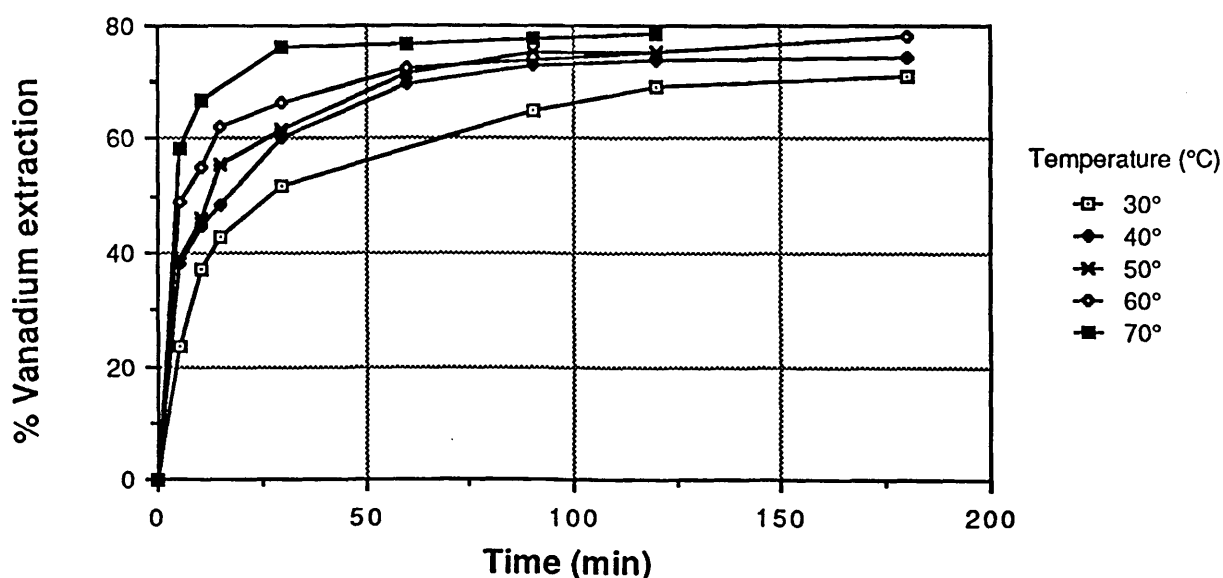
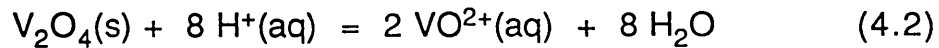


Figure 4.3 Effect of leaching temperature on the vanadium extraction from ground Flexicoke; $-53\mu\text{m}$ ground coke, 550 rpm stirring speed and $1\text{M H}_2\text{SO}_4$.

The data given in Figure 4.3 can be fitted into a kinetic model. The chosen model was the familiar shrinking core model, described by Equation 4.1 below:

$$1 - (2/3)\alpha - (1-\alpha)^{2/3} = \frac{2 C V_m D_E t}{\sigma r_0^2} \quad (4.1)$$

where α is the fraction of metal in solution; C is the leachant concentration; V_m is the molecular volume of the vanadium species in Flexicoke, assumed to be V_2O_4 ; D_E is the effective diffusion coefficient; r_0 the average particle radius; σ the stoichiometric factor and t the time. The reaction of interest is:



The shrinking core model is often used to describe the reaction kinetics obtained when the product of a reaction deposits on the reaction interface, and diffusion through the product layer becomes rate controlling. In Flexicoke leaching, the particle is essentially inert (carbon), and as the leaching reaction proceeds an unreacted core is obtained with a reacted diffusion layer surrounding it.

Flexicoke particles are essentially not porous, thus, the effect of grinding the coke is two-fold: firstly to liberate the vanadium species so that direct contact between the acid and the metal value can take place; and secondly, to provide a network of cracks, produced by the violent grinding process, through which the liquid reactant can diffuse into the particle. This is reflected by the increase in specific surface area from 2.53 to 45.64 m²/g in grinding the coke to -53 μ m (this is an eighteen times increase in surface area as compared to the expected increase of seven times from size reduction).

In applying the shrinking core model the following assumptions were made:

a) The particles were essentially spherical, of the same size, and their radius, r_0 , remained constant throughout the reaction.

b) The bulk concentration of the leachant did not change during the leaching reaction (this assumption was supported by the fact that the pH of the leachant remained constant throughout the experiment); and its concentration at the reaction interface was small compared to the bulk concentration.

c) The vanadium distribution is uniform throughout the Flexicoke particle. This assumption is clearly not valid for as-received Flexicoke, but in ground Flexicoke the vanadium concentration will be high for some particles and low for others, giving, on average, a uniform concentration. This assumes random breakage of particles during grinding.

Figure 4.4 shows that the shrinking core model is applicable to the vanadium extraction data up to about 70% extraction. Above that the extraction rate slows down, equilibrium is reached and the model breaks down. The slope of the lines shown in Figure 4.4 were found by the method of least squares, with the best line being forced through the origin, as required by equation 4.1. Regression coefficients higher than 88% were found in all cases.

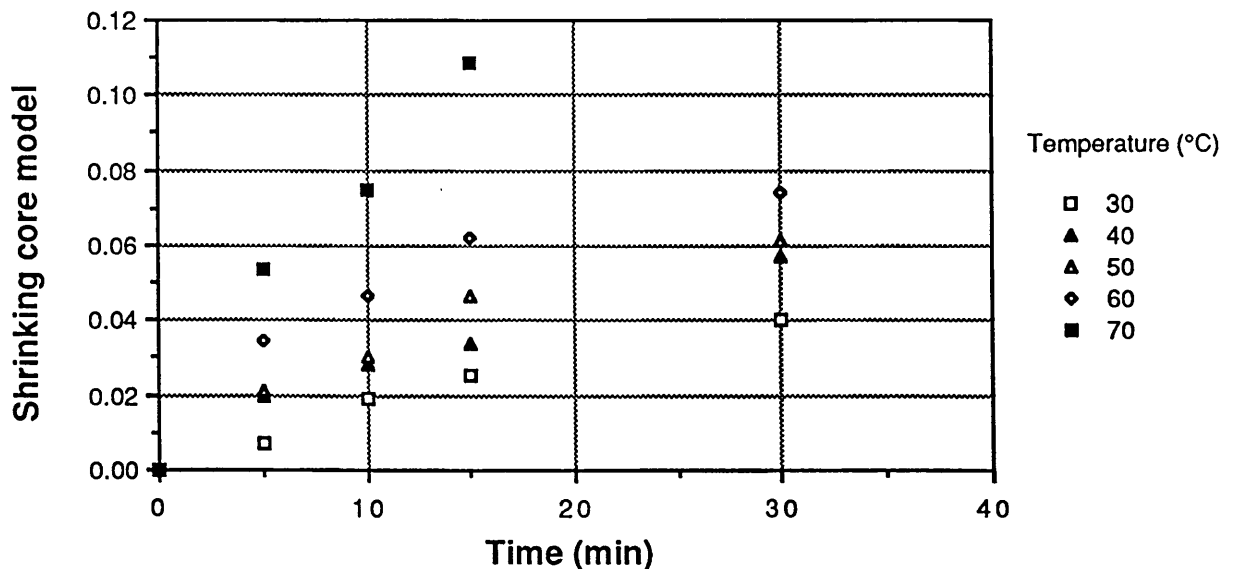


Figure 4.4 Effect of leaching temperature on the kinetics of vanadium extraction from Flexicoke; (-53 μ m ground coke, 550 rpm stirring speed and 1M H₂SO₄).

The slopes obtained from Figure 4.4 are proportional to the effective diffusion coefficient, and are given by Equation 4.3 below:

$$\text{Slope} = \frac{2 C V_m D_E}{\sigma r_0^2} \quad (4.3)$$

Clearly, the only temperature dependent variable in Equation 4.3 is the diffusion coefficient, and this dependence can be described by a classical Arrhenius type equation. Figure 4.5 shows that the Arrhenius law is indeed obeyed and the activation energy for vanadium extraction to be 23.9 kJ/mol. It is generally agreed that the activation energy for a diffusion controlled reaction is less than 20 kJ/mol, whilst that of chemically controlled reaction falls in the range of 40 to 100 kJ/mol. Thus, the experimentally obtained activation energy refers to a mixed kinetics situation, where the rate controlling steps are diffusion through the reacted coke layer and boundary layer diffusion and/or chemical kinetics.

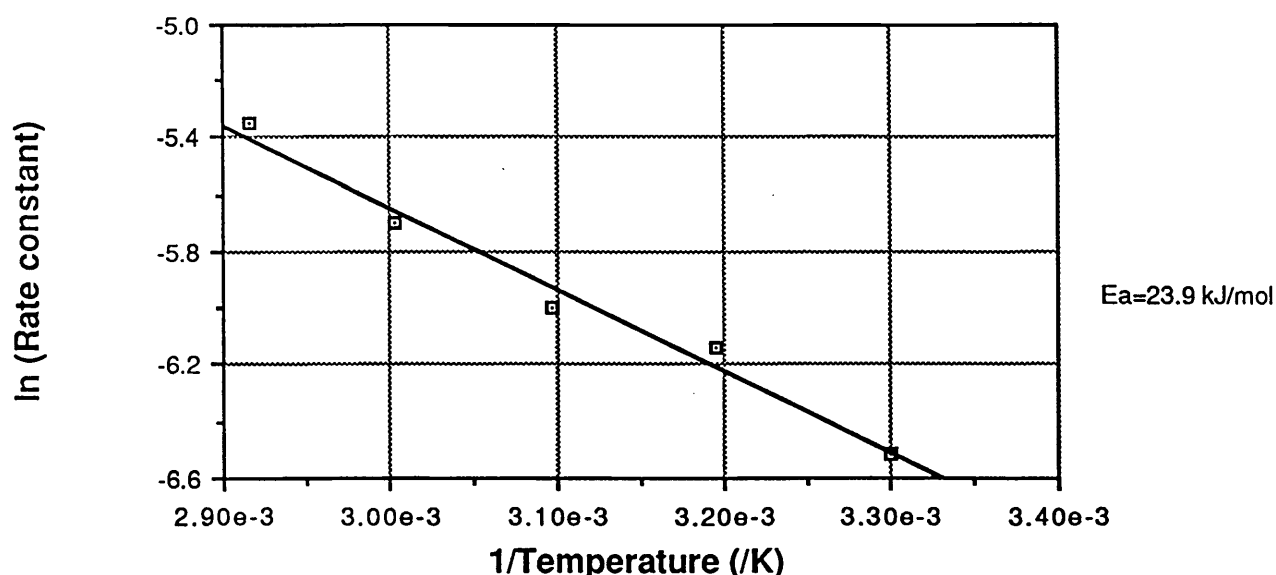


Figure 4.5 Arrhenius plot for vanadium extraction from ground Flexicoke; (-53 μ m coke, 550 rpm stirring speed and 1M H₂SO₄).

4.2.2 Effect of acid concentration.

Figure 4.6 shows the effect of sulphuric acid concentration on the vanadium extraction from ground Flexicoke at 40°C. The given data has been averaged from the results obtained from two runs. The results showed a scatter of up to $\pm 10\%$ on the maximum vanadium extraction. The standards used for atomic absorption spectroscopy analysis were prepared in the same acid concentration as used in the leaching runs so as to eliminate viscosity errors during analysis. Figure 4.6 shows that the vanadium extraction from ground Flexicoke increases with increasing acid concentration, reaches a maximum at a sulphuric acid concentration of 1 M, and then drops with further increases in the acid concentration. Nickel extractions were low and ranged from 3.5 to 8%. The acid concentration appeared to have little effect on the nickel extraction.

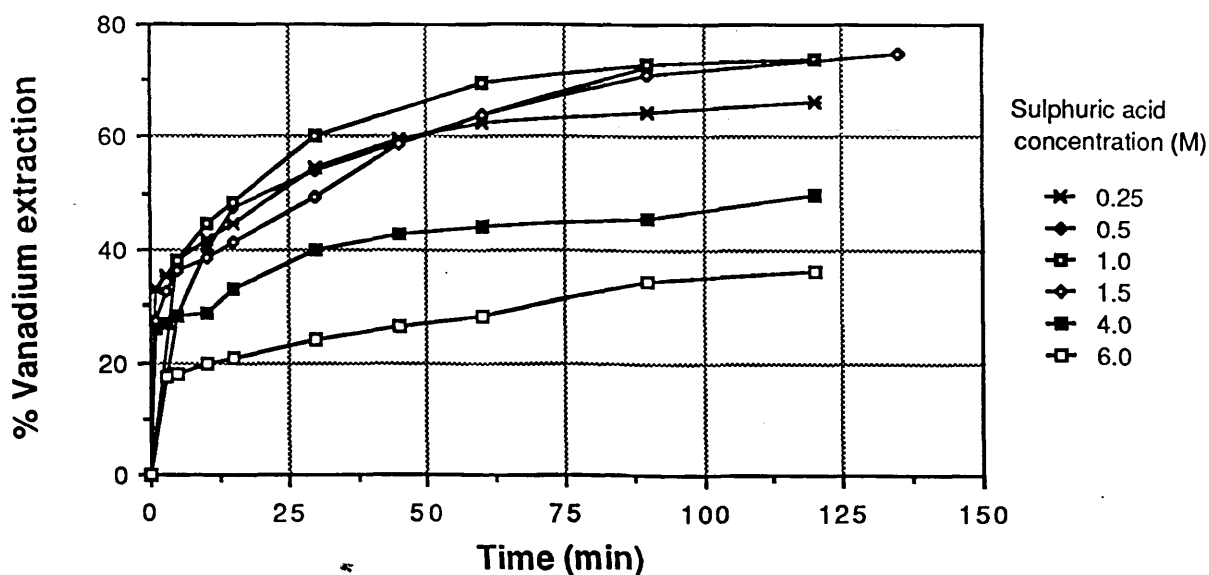


Figure 4.6 Effect of sulphuric acid concentration on the vanadium extraction from ground Flexicoke; (-53 μm ground coke, temperature=40°C and 550 rpm agitation speed).

The vanadium extraction rate, as defined by the shrinking core model, also showed a similar effect to the extraction behaviour at different sulphuric acid concentrations. Figure 4.7 shows that the extraction rate increases with increases in acid concentration, reaches a maximum when the acid concentration is 1 M, and then drops with further increases in the acid concentration.

This unusual extraction behaviour may be due to one, or a combination of the following reasons:

- a) Changes in complex stability at different acid concentrations.
- b) Changes in vanadium solubility with changes in acid concentration.
- c) Changes in diffusivity due to the increase in viscosity with increase in the acid concentration.

Appendix A gives the results from a spectrophotometric study of vanadium (V) and vanadium (IV) complexes in sulphuric acid. UV spectral analysis of the leach liquors revealed vanadium to be present as the VO^{2+} cation; within the limits of detection (about 1 ppm) no VO_2^+ was found. From Appendix A it can be seen that the sulphate complexes of vanadium (IV) are more stable than the bisulphate complexes (probably because the sulphate ion is acting as a bidentate ligand), thus, the system of interest in this work is the $\text{VO}^{2+}\text{-SO}_4^{2-}$ system.

Figure 4.8 below shows the data given in Figure A13 (Appendix A) recalculated to show the molar fraction for a given complex, α , versus the sulphuric acid concentration. From this figure it can be seen that α for the VOSO_4 complex shows a similar behaviour to that shown by vanadium extraction; i.e. the fraction of VOSO_4 rises as the acid concentration increases, reaches a maximum at about 1 M H_2SO_4 and then falls with further increases in the acid concentration. A reasonably good fit is obtained between the vanadium extraction rate and the fraction of VOSO_4 , Figure 4.9, considering that the α data was measured at 18°C and the extraction rates at 40°C. At higher

temperatures the value of the first stepwise stability constant, K_1 , for the $\text{VO}^{2+}\text{-SO}_4^{2-}$ system will decrease and the maximum for the VOSO_4 complex will shift towards higher sulphuric acid concentrations, and a better fit would be obtained.

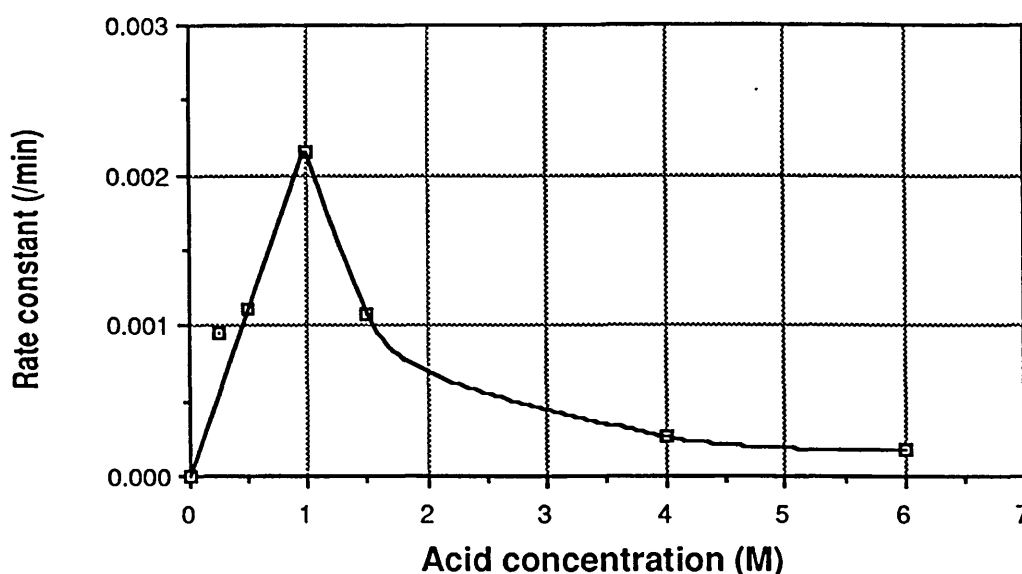


Figure 4.7 Effect of acid concentration on the rate of vanadium extraction from ground Flexicoke; $-53\mu\text{m}$ Flexicoke, temperature 40°C , 550 rpm agitation speed.

Measurements of the zeta potential are unreliable below pH 1.5 because of the high ionic strength of the solutions, however, the point of zero charge (pzc) for ground Flexicoke was determined to fall between pH 0 to 0.5. Therefore, at the very low pH of the leaching solutions the surface of the coke would be expected to be positively charged from the absorption of H^+ ions. As the coke is leached the cationic complex VO^{2+} , the neutral VOSO_4 complex and the anionic complex $\{\text{VO}(\text{SO}_4)_2\}^{2-}$ are extracted into the bulk solution; however, because of the positive charge on the coke surface the anionic species are absorbed onto the coke. Thus, the vanadium extraction appeared to decrease with increasing sulphuric acid concentration because of the increase in the mole fraction of anionic complexes in solution.

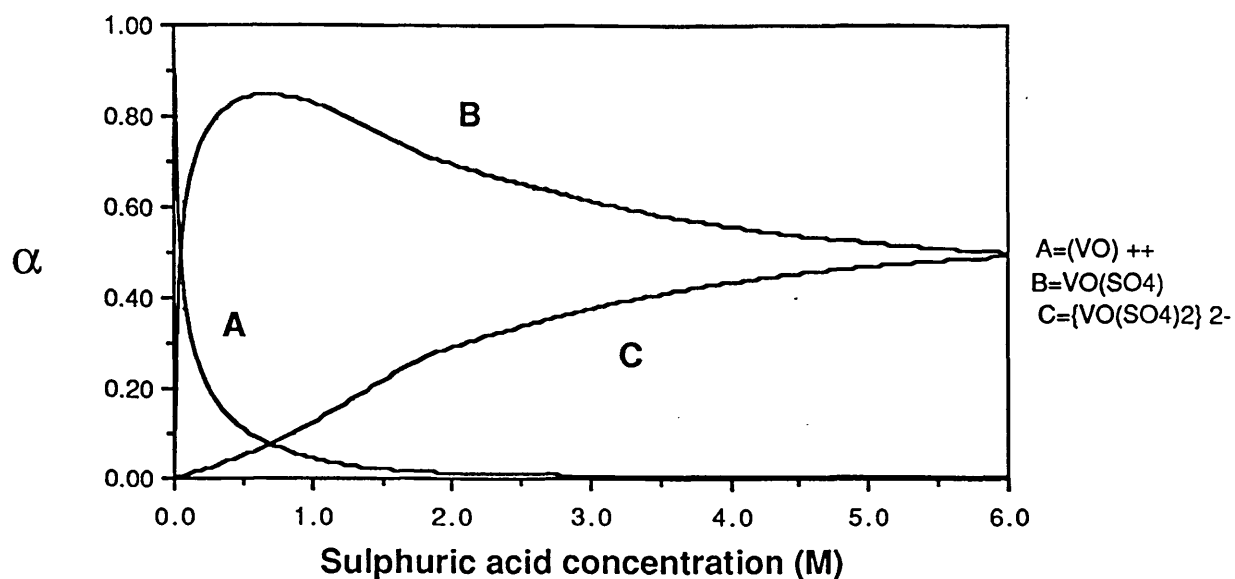


Figure 4.8 Distribution of complexes for the VO^{2+} - SO_4^{2-} system as a function of the sulphuric acid concentration.

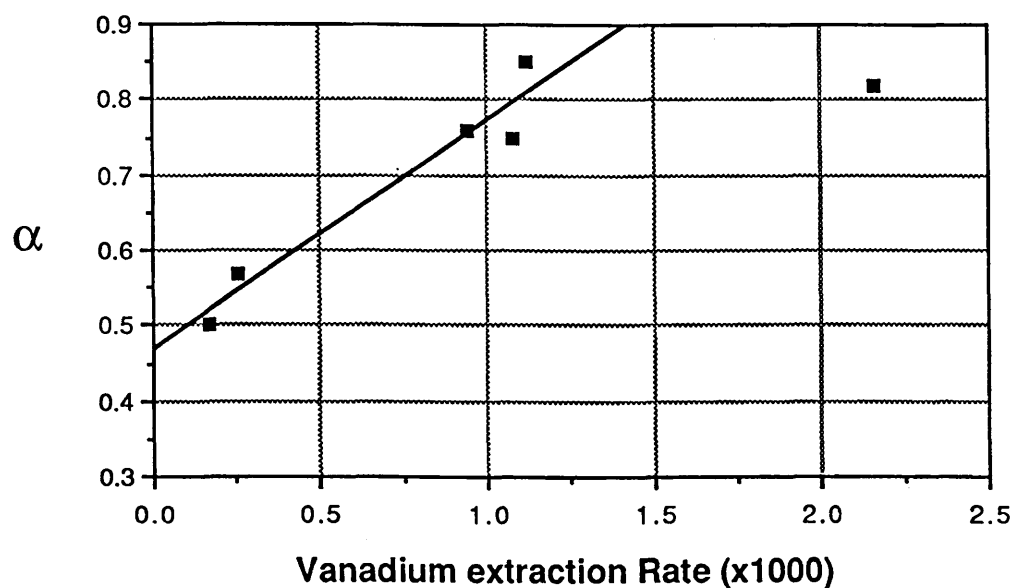


Figure 4.9 Vanadium extraction rate from Flexicoke versus the mole fraction of the VOSO_4 complex.

An experiment was performed in which a sample of ground Flexicoke was leached with 4 M H_2SO_4 solution for 2 hours at 18°C . The coke was then filtered and washed with 4 M H_2SO_4 , followed by filtration, washing with distilled water, filtration and finally two washings with 4 M NaOH solution. The aim of the experiment was to test whether on raising the solution pH, and thus making the charge on the coke surface negative, the absorbed anionic complexes would be released into solution. The acid wash ensures that little of the leach liquor remains on the coke. The filtered leach liquor was a deep blue colour; the water filtrate was pale blue, and the NaOH filtrates were a deep brown colour. The results from atomic absorption analysis of the leach liquor and filtrates were:

Leach liquor + acid filtrate = 9.6×10^{-3} M of vanadium.

Distilled water filtrate = 7.1×10^{-4} M of vanadium.

4 M NaOH filtrates = 4.6×10^{-3} M of vanadium.

The very high vanadium concentration in the NaOH filtrate would not be expected unless the anionic complexes were being desorbed from the surface by substitution by OH^- ions. If the vanadium complexes in the NaOH and water filtrates are assumed to be the anionic sulphate complexes, and those in the leach liquor are the neutral and positive complexes, then the mole fractions of neutral plus cationic and anionic complexes were 0.63 and 0.37, respectively. From Figure 4.8, mole fractions of 0.56 and 0.44 for the cationic plus neutral complexes and the anionic complexes, respectively, would be expected. The agreement is excellent considering the simplicity of the experiment and the few washes used.

The solubility for vanadium (V) oxide and vanadium (IV) sulphate in different sulphuric acid concentrations was investigated and the results are shown in Figure 4.10 below. As can be seen, at low sulphuric acid concentrations vanadium (IV) sulphate is far more soluble than vanadium (V) oxide; the solubility of VOSO_4 decreases with increasing sulphuric acid concentration whilst

that of V_2O_5 increases slightly but decreases at very high H_2SO_4 concentration. As none of the leach liquors approached the saturation concentrations, it can be safely concluded that the decrease in vanadium extraction with increasing acid concentration is due to the formation of anionic complexes which get absorbed by the positively charged coke surface. This was a simple solubility test, and no checks were made to ensure that the solutions were not over saturated; the values given in Figure 4.10 are the vanadium concentrations found in solution once the added powder failed to dissolve one week after addition. The kinetics of dissolution were slow; a 0.5 gramme sample of V_2O_5 generally required 2-3 days to fully dissolve; dissolution of the $VOSO_4$ was faster.

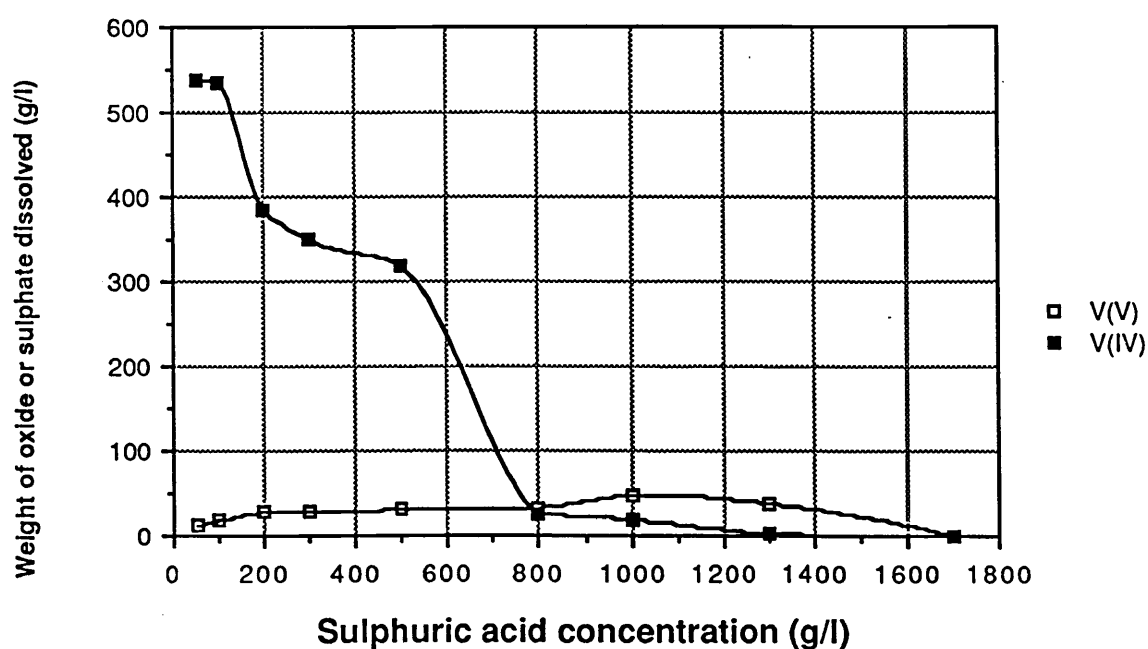


Figure 4.10 Effect of sulphuric acid concentration on the solubility of vanadium (V) oxide and vanadium (IV) sulphate at 25°C.

4.2.3 Effect of agitation speed.

Figure 4.11 below shows the effect of agitation speed on the vanadium extraction from -53 μ m ground Flexicoke, at 40°C with 1 M sulphuric acid. The agitation speed had no effect on the vanadium yield in the agitation speed range between 550 and 1200 rpm.

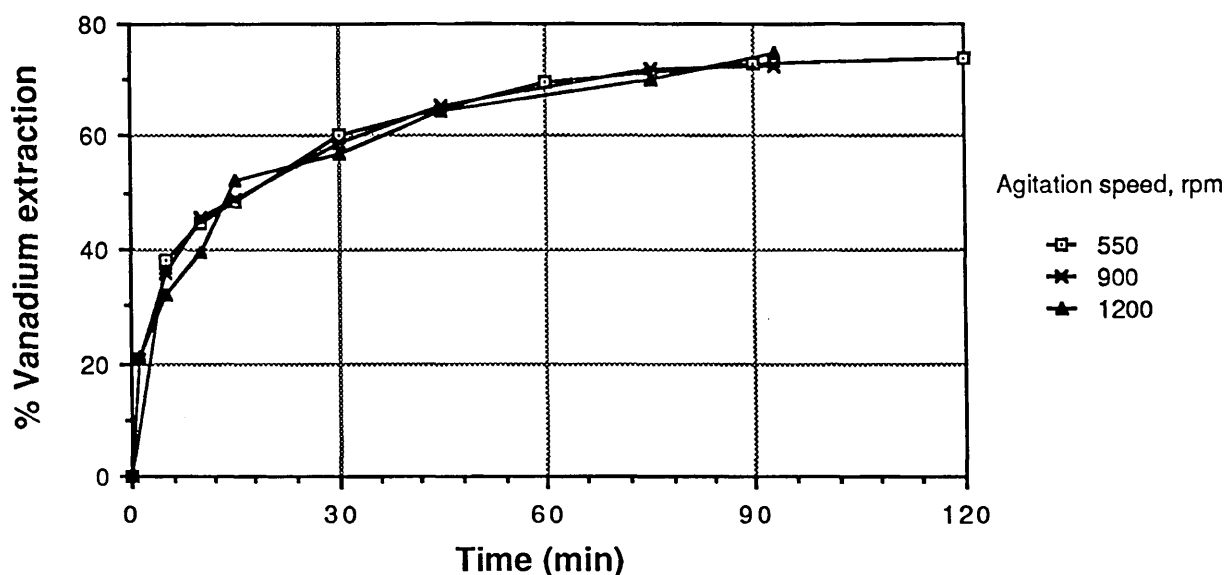


Figure 4.11 Effect of agitation speed on the vanadium extraction from leaching ground Flexicoke; -53 μ m ground Flexicoke 1M H₂SO₄, temperature=40°C.

4.2.4 Effect of particle size.

Figure 4.12 below shows the effect of particle size of the vanadium extraction from ground Flexicoke at 40°C with 1 M sulphuric acid. As can be seen grinding the coke has a very big effect on the maximum extraction.

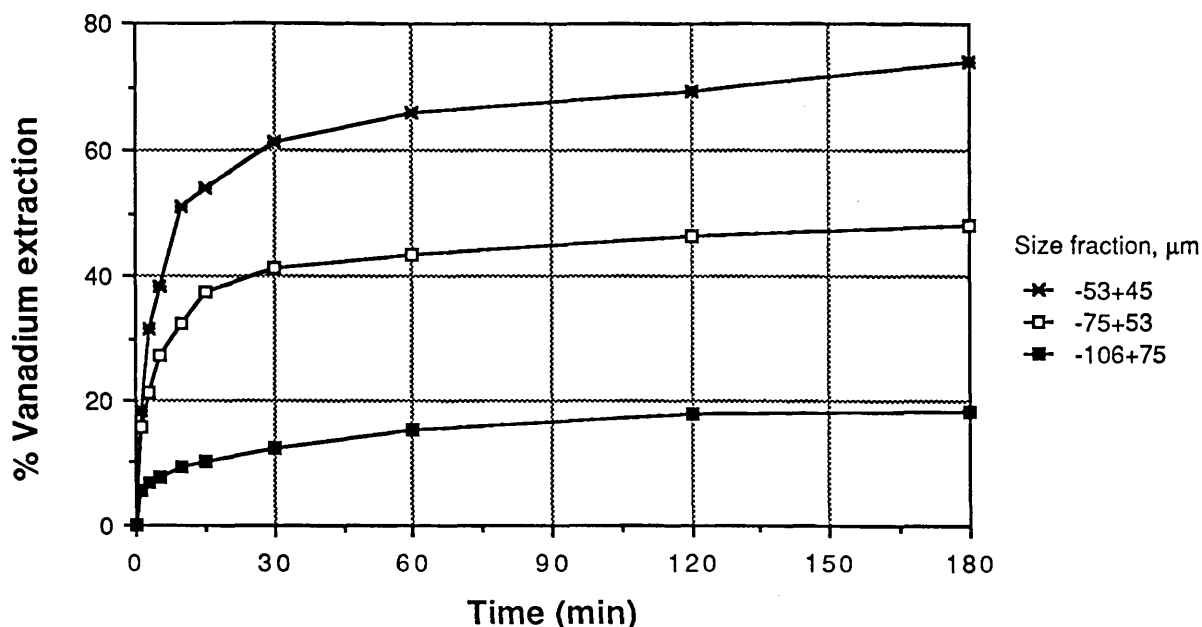


Figure 4.12 Effect of particle size on the vanadium extraction from ground Flexicoke; temperature=40°C, 1M H₂SO₄, agitation speed=550 rpm.

From equation 4.1 the rate of vanadium extraction would be expected to be inversely proportional to the square of the particle radius. Figure 4.13 below gives a plot of the extraction rate versus the inverse of the average particle size squared, and a straight line is indeed obtained. The average particle radius was found by calculating the arithmetical mean of the two sieve sizes used for each size fraction.

4.3 LEACHING OF DELAYED COKE.

As-received delayed coke has been leached with 1 M sulphuric acid with and without the use of a surfactant. At 80°C and after 19 hours of leaching only trace amounts of vanadium and nickel could be detected. Grinding of the coke to -53μm did not improve the metal extraction. The use of organic leaching reagents was also tried, the results of which are given in Table 4.3 below. Although there seemed to be considerable interaction

between the coke and the solvent, very little vanadium was extracted (around 0.01%). Nickel and iron could not be detected in solution.

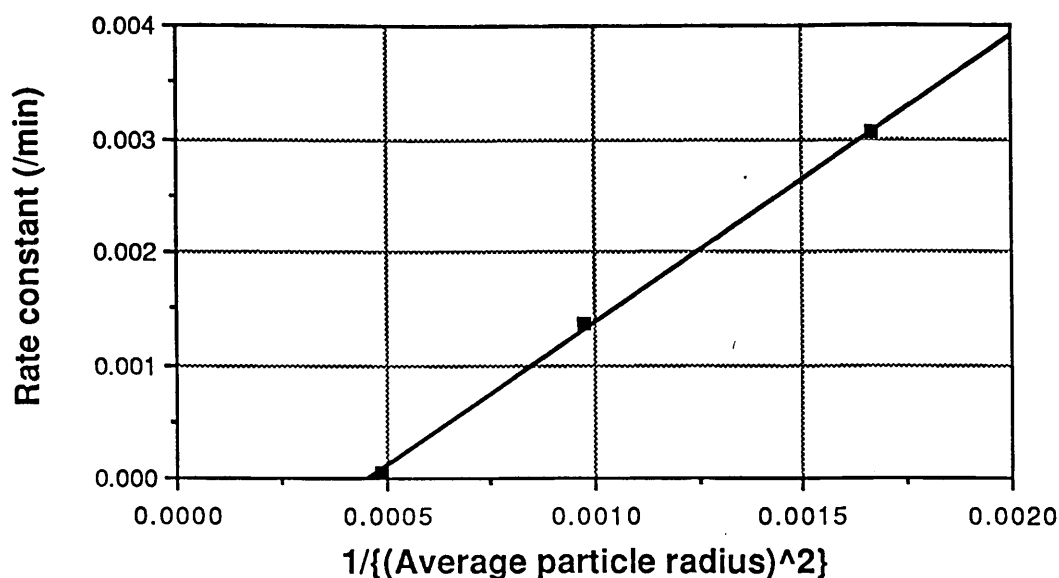


Figure 4.13 Plot of the vanadium extraction rate from the shrinking core model versus the inverse of the square of the average particle radius; radius measured in μm .

Solvent	% Coke dissolution	Time (hours)	% Vanadium extraction	Observations
Dichloromethane	14.0	24	Trace	Amber solution
DMF	9.1	96	Trace	Amber solution
Toluene	2.5	96	Trace	Amber solution
DMSO	10.2	96	Trace	Amber solution
Quinoline	N/A	96	Trace	Amber solution
Benzene	8.6	96	Trace	Amber solution

Table 4.3 Vanadium extraction and coke dissolution by organic solvents from Delayed coke.

Delayed coke was thus not amenable to chemical attack. The reason for its the low metal extractions could be that the metal values are locked in the form of a large organic molecule. The lower temperatures used during the production of Delayed coke, as compared to Flexicoke, are apparently insufficient to completely break these structures. Delayed coke has a much higher heteroatom to metal ratio than Flexicoke, giving further evidence that the highly aromatic, multidentate ligands surrounding the metal ions are still present in Delayed coke. Some of the extracts obtained from the reaction of the organic solvent with Delayed coke were analysed by infrared spectrophotometry and the results are given in Table 4.4.

Furthermore, Delayed coke was found to have low specific surface area of 0.73 m²/g. This is about 3.5 times smaller than in as-received Flexicoke.

Solvent	Coke	Absorption band, cm ⁻¹	Assignment
Quinoline	F	3400	a) Secondary alcohols b) Aromatic secondary amine ([C ₆ H ₆]-NH-R)
		1670	a) Amides (CO-NH-R or CO-N-R ₂)
DMSO	F	3400	As for Quinolene
		1670	As for Quinolene
		1200	a) Substituted aromatic b) Tertiary alcohol c) Esters d) Tertiary amines e) Aromatic esters
		990	a) Aromatic substituted b) Aromatic esters
		810	a) Substituted Aromatics
DMSO	D	3400	As for Quinolene
		1740	a) Secondary and tertiary amides b) Nitrites (R-O-NC)
		1670	As for Quinolene
		1200	As for DMSO (Flexicoke)
		810	As for DMSO (Flexicoke)

Table 4.4 Infrared bands from the analysis of extracts obtained by reaction of organic solvents with Flexicoke and Delayed coke; F=Flexicoke; D=Delayed coke.

Solvent	Coke	Absorption band	Assignment
Dichloromethane	D	3040	a) C-H stretching band.
		1675	Existing band in pure solution dissapeared
		1200	As for DMSO
DMF	F	3540	a) As for 3400 Quinoline.
		760	a) C-H bending.
DMF	D	3540	a) As for DMF (Flexicoke).
		760	a) As for DMF (Flexicoke).
Benzene	F	N/D	-
Benzene	D	N/D	-
Toluene	F	N/D	-
Toluene	F	N/D	-

Table 4.4 (Continued) Infrared bands from the analysis of extracts obtained by reaction of organic solvents with Flexicoke and Delayed coke; F=Flexicoke; D=Delayed coke; N/D= non-detected.

5. VAPOUR TRANSPORT EXPERIMENTS. RESULTS AND DISCUSSION.

5.1 THERMODYNAMIC STUDY.

In order to determine whether the vanadium and nickel species in Flexicoke could be extracted by a vapour transport process in which the metal values react with a chloride source at high temperature, producing a volatile metal chloride which vaporizes and is transported by a flowing gas stream onto the cooler parts of a furnace, a brief thermodynamic study was conducted. The best way of displaying such data is in the form of Ellingham diagrams given in Figures 5.1, 5.2, 5.3 and 5.4 below. The key for these Figures is given in Table 5.1.

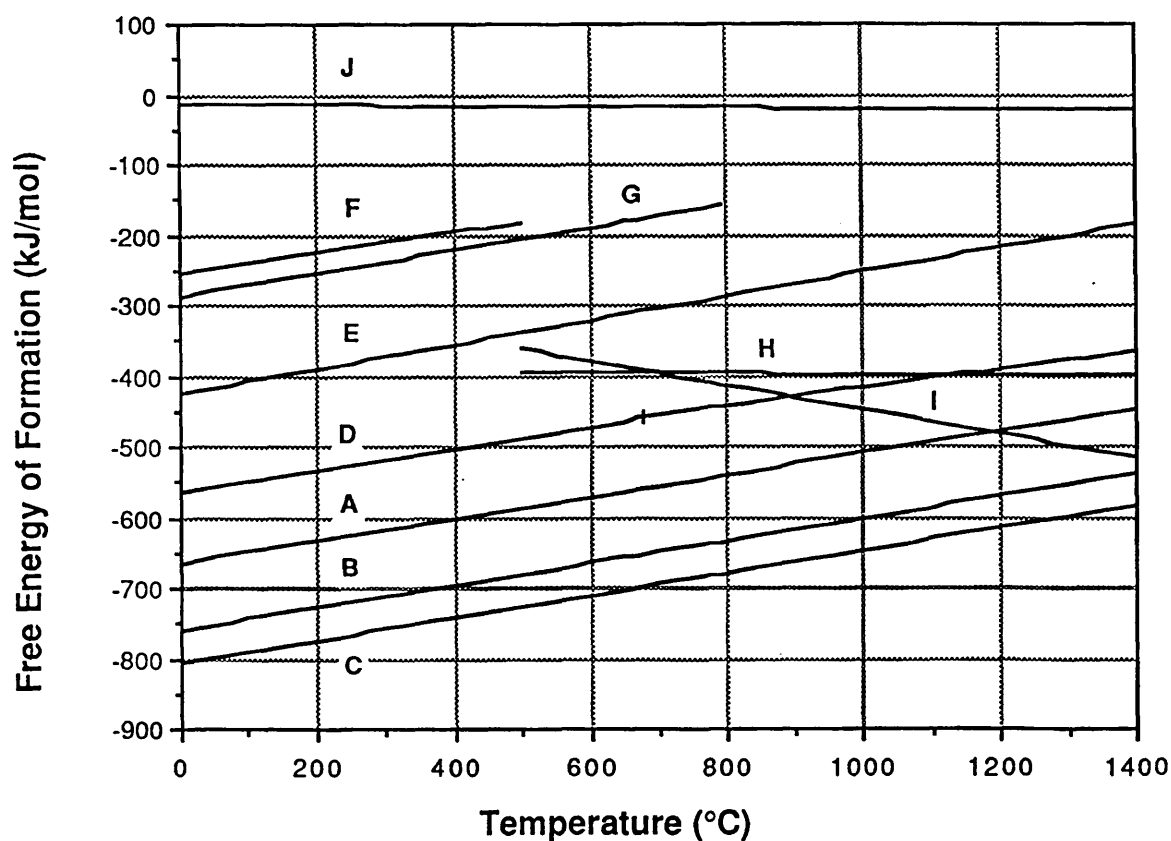


Figure 5.1 Standard free energies of formation of some vanadium and nickel oxides and sulphides as a function of temperature.

Reaction code	Reaction	ΔH (kJ/mol)	$-\Delta S$ (J/°C mol)	Temperature range (°C)	Ref
A	$[V] + (O_2) = [VO_2]$	-168.8	37.12	25-1360	T
B	$4/3 [V] + (O_2) = 2/3 [V_2O_3]$	-191.7	37.85	25-2070	T
C	$2 [V] + (O_2) = 2 [VO]$	-203.0	38.26	25-1800	T
D	$2/5 [V] + (O_2) = 2/5 [V_2O_5]$	-200.0	37.28	25-670	T
	$2/5 [V] + (O_2) = 2/5 \{V_2O_5\}$	-138.4	30.74	670-2000	T
E	$2 [Ni] + (O_2) = [NiO]$	-112.6	41.14	25-1984	T
F	$2 [Ni] + (S_2) = 2 [NiS]$	-70.0	34.40	25-500	T
G	$3 [Ni] + (S_2) = [Ni_3S_2]$	-79.2	39.01	25-790	T
H	$[C] + (O_2) = (CO_2)$	-94.5	-0.13	500-2000	T
I	$2 [C] + (O_2) = 2 (CO)$	-54.7	-41.00	500-2000	T
J	$[C] + (S_2) = (CS_2)$	-2.7	-1.55	25-2000	T
K	$1/2 [V] + (Cl_2) = 1/2 \{VCl_4\}$	-68.1	26.24	25-152	K
	$1/2 [V] + (Cl_2) = 1/2 (VCl_4)$	-62.7	13.44	152-N/A	K/N
L	$2/3 [V] + (Cl_2) = 2/3 [VCl_3]$	-92.5	37.03	25-650	K
M	$[V] + (Cl_2) = [VCl_2]$	-108.0	37.00	Subl. 910	N
N	$2/3 [V] + (Cl_2) + 1/2 (O_2) = 2/3 \{VOCl_3\}$	-117.1	35.30	25-127	N
	$2/3 [V] + (Cl_2) + 1/2 (O_2) = 2/3 (VOCl_3)$	-110.9	19.39	127-N/A	N

Table 5.1 Key and data used in drawing the Ellingham diagrams.

[X]=Solid; {X}=liquid; (X)=gas. References: T=[101]; K=[127]; N=[128].

Reaction code	Reaction	ΔH (kJ/mol)	$-\Delta S$ (J/°C mol)	Temperature range (°C)	Ref
O	$[\text{Ni}] + (\text{Cl}_2) = [\text{NiCl}_2]$	-73.0	35.00	25-987	T
	$[\text{Ni}] + (\text{Cl}_2) = (\text{NiCl}_2)$	-19.2	-7.70	987-1453	T
P	$2 (\text{VCl}_4) = 2 [\text{VCl}_3] + (\text{Cl}_2)$	-27.0	57.31	25-650	N
Q	$2 [\text{VCl}_3] = [\text{VCl}_2] + (\text{VCl}_4)$	44.3	-47.20	25-650	N
R	$(\text{H}_2) + (\text{Cl}_2) = 2 (\text{HCl})$	-45.0	3.06	25-2000	T
S	$1/4 [\text{VO}_2] + (\text{HCl}) = 1/4 (\text{VCl}_4) + 1/2 (\text{H}_2\text{O})$	3.8	2.57	152-N/A	T/K
T	$1/4 [\text{VO}_2] + (\text{HCl}) + 1/2 [\text{C}] = 1/4 (\text{VCl}_4) + 1/2 (\text{CO}) + 1/2 (\text{H}_2)$	19.7	-29.28	152-N/A	T/K
U	$1/3 [\text{VO}_2] + (\text{HCl}) = 1/3 (\text{VCl}_3) + 1/3 (\text{H}_2\text{O}) + 1/6 (\text{O}_2) + 1/6 (\text{H}_2)$	12.8	-4.31	25-650	T/N/K
V	$1/3 [\text{VO}_2] + (\text{HCl}) + 2/3 [\text{C}] = 1/3 (\text{VCl}_3) + 2/3 (\text{CO}) + 1/2 (\text{H}_2)$	14.3	-32.38	25-650	T/N/K
W	$1/3 [\text{VO}_2] + (\text{HCl}) = 1/3 (\text{VOCl}_3) + 1/3 (\text{H}_2\text{O}) + 1/6 (\text{H}_2)$	3.6	-4.96	127-N/A	T/N/K
X	$1/3 [\text{VO}_2] + (\text{HCl}) + 1/3 [\text{C}] = 1/3 (\text{VOCl}_3) + 1/3 (\text{CO}) + 1/2 (\text{H}_2)$	14.2	-26.19	127-N/A	T/N/K
Y	$1/8 [\text{V}_2\text{O}_5] + (\text{HCl}) = 1/4 (\text{VCl}_4) + 1/2 (\text{H}_2\text{O}) + 1/16 (\text{O}_2)$	24.1	-2.87	25-670	T/K
	$1/8 \{\text{V}_2\text{O}_5\} + (\text{HCl}) = 1/4 (\text{VCl}_4) + 1/2 (\text{H}_2\text{O}) + 1/16 (\text{O}_2)$	22.2	-0.83	670-2000	T/K
Z	$1/8 [\text{V}_2\text{O}_5] + (\text{HCl}) + 5/8 [\text{C}] = 1/4 (\text{VCl}_4) + 5/8 (\text{CO}) + 1/2 (\text{H}_2)$	36.6	-37.28	25-670	T/K
	$1/8 \{\text{V}_2\text{O}_5\} + (\text{HCl}) + 5/8 [\text{C}] = 1/4 (\text{VCl}_4) + 5/8 (\text{CO}) + 1/2 (\text{H}_2)$	34.7	-35.24	670-2000	T/K
AA	$1/6 [\text{V}_2\text{O}_5] + (\text{HCl}) = 1/3 (\text{VOCl}_3) + 1/2 (\text{H}_2\text{O})$	20.8	-0.69	127-670	T/N/K
	$1/6 \{\text{V}_2\text{O}_5\} + (\text{HCl}) = 1/3 (\text{VOCl}_3) + 1/2 (\text{H}_2\text{O})$	18.3	2.02	670-2000	T/N/K

Table 5.1 (Continued) Key and data used in drawing the Ellingham diagrams.

[X]=Solid; {X}=liquid; (X)=gas. References: T=[101]; K=[127]; N=[128].

Reaction code	Reaction	ΔH (kJ/mol)	$-\Delta S$ (J/°C mol)	Temperature range (°C)	Ref
AB	$1/6 [V_2O_5] + (HCl) + 1/2 [C] = 1/3 (VOCl_3) + 1/2 (CO) + 1/2 (H_2)$	36.7	-32.54	127-670	T/N/K
	$1/6 \{V_2O_5\} + (HCl) + 1/2 [C] = 1/3 (VOCl_3) + 1/2 (CO) + 1/2 (H_2)$	34.2	-29.83	670-2000	T/N/K
AC	$1/6 [V_2O_5] + (HCl) = 1/3 (VCl_3) + 1/2 (H_2O) + 1/2 (O_2)$	30.0	-0.07	25-650	T/N/K
AD	$1/6 [V_2O_5] + (HCl) + 5/6 [C] = 1/3 (VCl_3) + 5/6 (CO) + 1/2 (H_2)$	36.8	-38.75	25-650	T/N/K
AE	$1/2 [NiS] + (HCl) = 1/2 (NiCl_2) + 1/2 (H_2S)$	19.4	-7.94	25-500	T
AF	$1/4 [Ni_2S_3] + (HCl) = 1/2 (NiCl_2) + 1/2 (H_2S) + 1/8 (S_2)$	17.9	-14.94	25-790	T/K
AG	$1/2 [NiO] + (HCl) = 1/2 (NiCl_2) + 1/2 (H_2O)$	11.5	-9.02	25-1453	T
AH	$1/2 [NiO] + (HCl) + 1/2 [C] = 1/2 (NiCl_2) + 1/2 (CO) + 1/2 (H_2)$	27.4	-40.86	25-1453	T

Table 5.1 (Continued) Key and data used in drawing the Ellingham diagrams.

[X]=Solid; {X}=liquid; (X)=gas. References: T=[101]; K=[127]; N=[128].

Figure 5.1 gives the free energies of formation of some vanadium and nickel oxides and sulphides. As already seen in Chapter 3 the vanadium species in the coke appear not to be associated with sulphur, thus only the oxides of vanadium were considered. At the maximum temperatures of reaction encountered in the Flexicoking process (800° to 1000°C) it can be seen that only V_2O_5 (reaction D) can be reduced by carbon; the other oxides have greater thermodynamic stability with respect to elemental vanadium and oxygen gas (reactions A, B and C). Nickel, on the other hand, is associated with the sulphur in the coke, and as seen in Figure 5.1, neither NiS (reaction F) nor Ni_2S_3 (reaction G) can be reduced by carbon because of the low stability of CS_2 (reaction J). Thus, it can be assumed that vanadium exists in the form of an oxide, probably V_2O_4 (the oxide VO_2 shown in Table 5.1 is the same as V_2O_4), and nickel in the form of a sulphide.

Figure 5.2 gives the free energies of formation of some vanadium chlorides and oxychlorides and nickel chloride. No thermodynamic data is available on gaseous VCl_3 and VCl_2 ; and none on $VOCl_2$, $VOCl$ and VO_2Cl (in any physical state) was found. As can be seen from Figure 5.2 the thermodynamic stability of the chlorides of vanadium increases as the number of chlorine atoms decreases (reactions K, L and M). $VOCl_3$ is more stable (reaction N) than the simple vanadium chlorides. VCl_4 is reported [117] to decompose to VCl_3 and Cl_2 (reaction P), and this is thermodynamically favourable below 200°C. VCl_3 is reported [117, 121] to disproportionate to VCl_4 and VCl_2 (reaction Q), however, above 650°C VCl_3 volatilizes (possibly above 450°C), thus lowering the entropy for reaction Q and reducing the degree of disproportionation. $NiCl_2$ is stable at all temperatures considered (reaction O); it sublimes at 987°C.

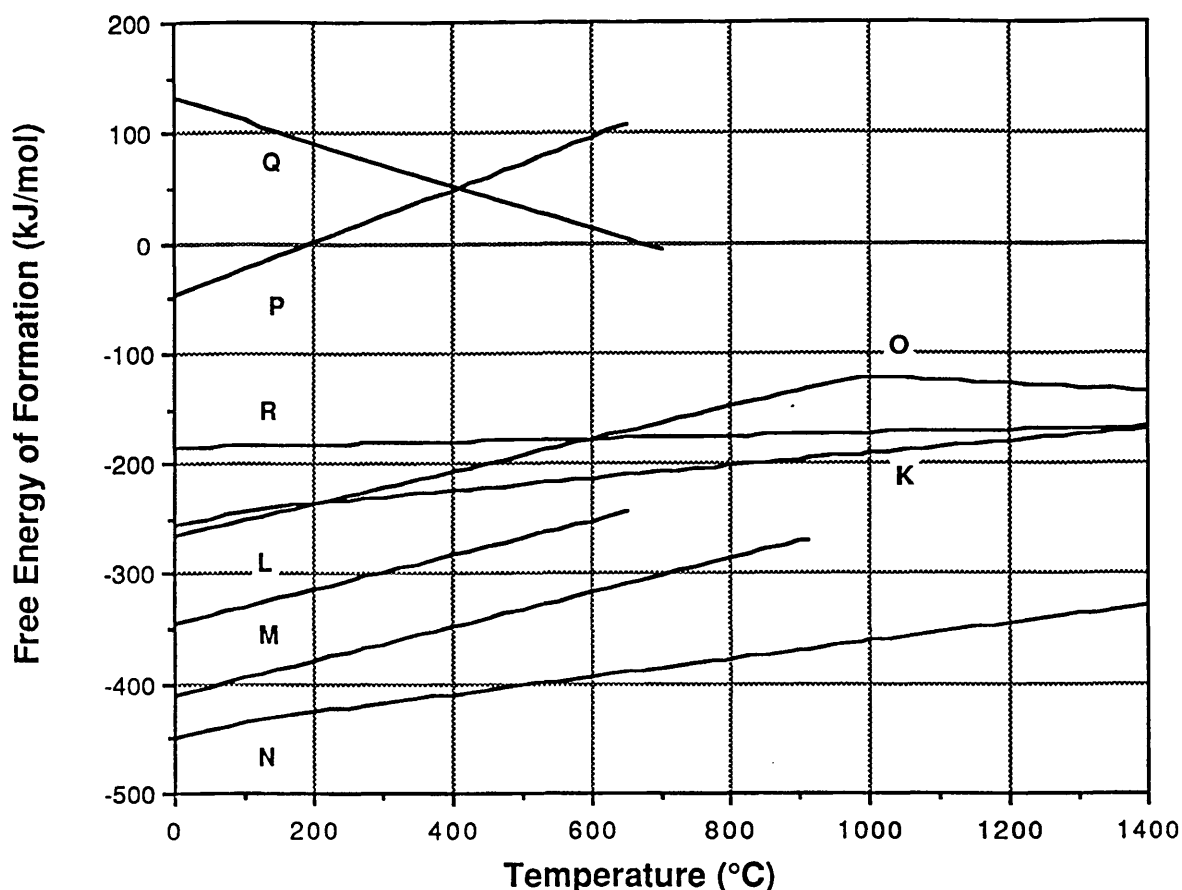


Figure 5.2 Standard free energies of formation of some vanadium chlorides and oxychlorides and nickel chloride as a function of temperature.

Figure 5.3 below gives the free energy of formation as a function of temperature for a number of possible reactions between vanadium oxides (V_2O_4 and V_2O_5) and hydrogen chloride gas. From this figure it can be seen that the formation of VCl_4 and VCl_3 (reactions S and U) from V_2O_4 , and the formation of VCl_4 , VCl_3 and $VOCl_3$ (reactions Y, AC and AA) from V_2O_5 , are thermodynamically unfavourable under the conditions studied. However, all these reactions (with the exception of reaction AD: the formation of VCl_3 from V_2O_5) become favourable if the reaction between water vapour (produced by the chlorination reaction) and carbon (from the coke) to produce carbon monoxide and hydrogen is taken into account. Thus, chlorination of V_2O_4 and V_2O_5 is favoured by the presence of

carbon. If the vanadium species in the coke is V_2O_5 then higher reaction temperatures are required than if the species is V_2O_4 , i.e. the free energy of formation of gaseous VCl_4 becomes negative at 400° and 700°C for the reaction of HCl gas, carbon and V_2O_4 and V_2O_5 , respectively. Nevertheless, higher temperatures increase the vapour pressure of the chlorides and hence improve the transport conditions.

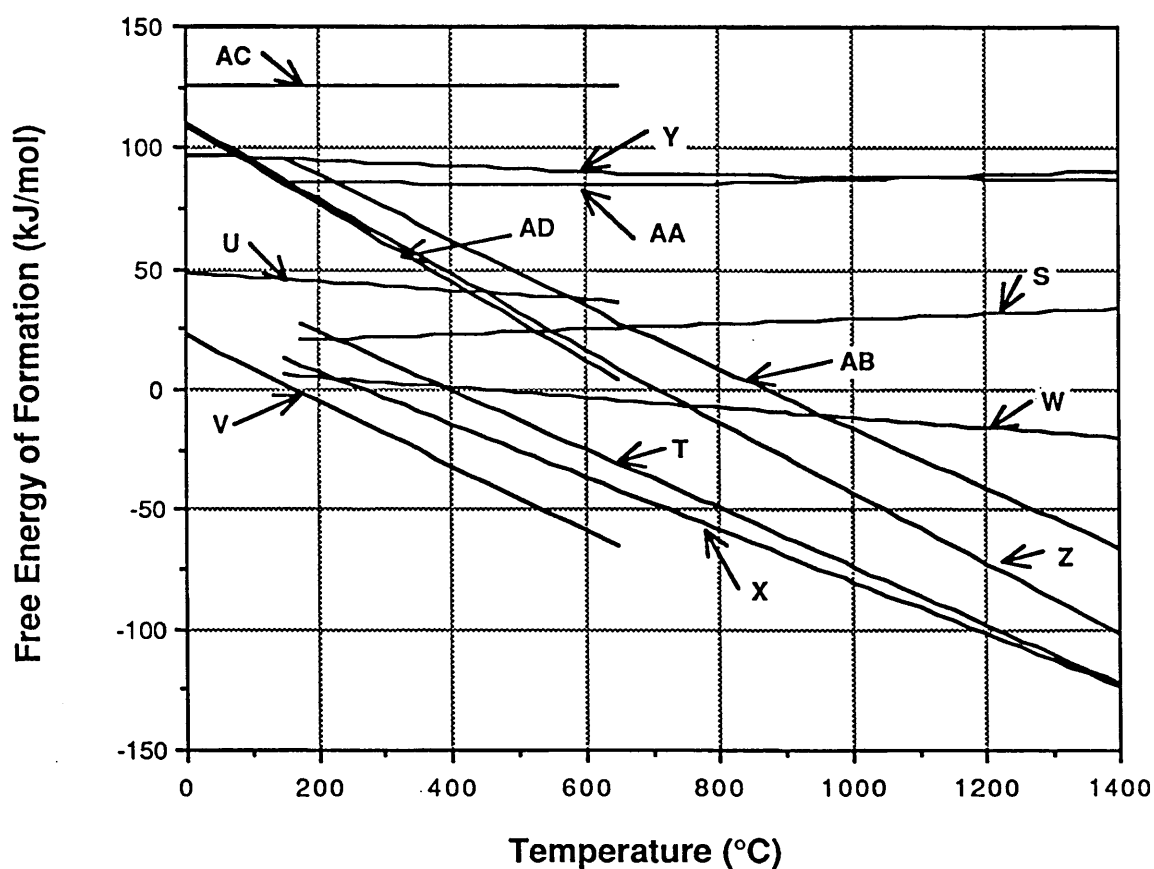


Figure 5.3 Standard free energies of formation for some reactions of interest in the vanadium oxide-hydrogen chloride system as a function of temperature.

Figure 5.4 below gives the free energy of formation for the reactions between nickel oxide and sulphides and hydrogen chloride gas as a function of temperature. As can be seen from Figure 5.4 the formation of gaseous $NiCl_2$ from NiS and Ni_2S_3 (reactions AE and AF, respectively) is thermodynamically

unfavourable. The data for Ni_2S_3 is valid up to 790°C , but if it were extrapolated to higher temperatures the free energy of formation of nickel chloride from Ni_2S_3 would become negative above 923°C . At temperatures below 284°C the reaction between NiS and HCl gas to form solid NiCl_2 also has a negative free energy. Thus, the formation of gaseous NiCl_2 from nickel sulphides is expected to be difficult, with high temperatures and high HCl partial pressures being required to increase the very low equilibrium partial pressure of gaseous NiCl_2 . The reaction between NiO and HCl is much more favourable (reaction AG), particularly in the presence of carbon (reaction AH).

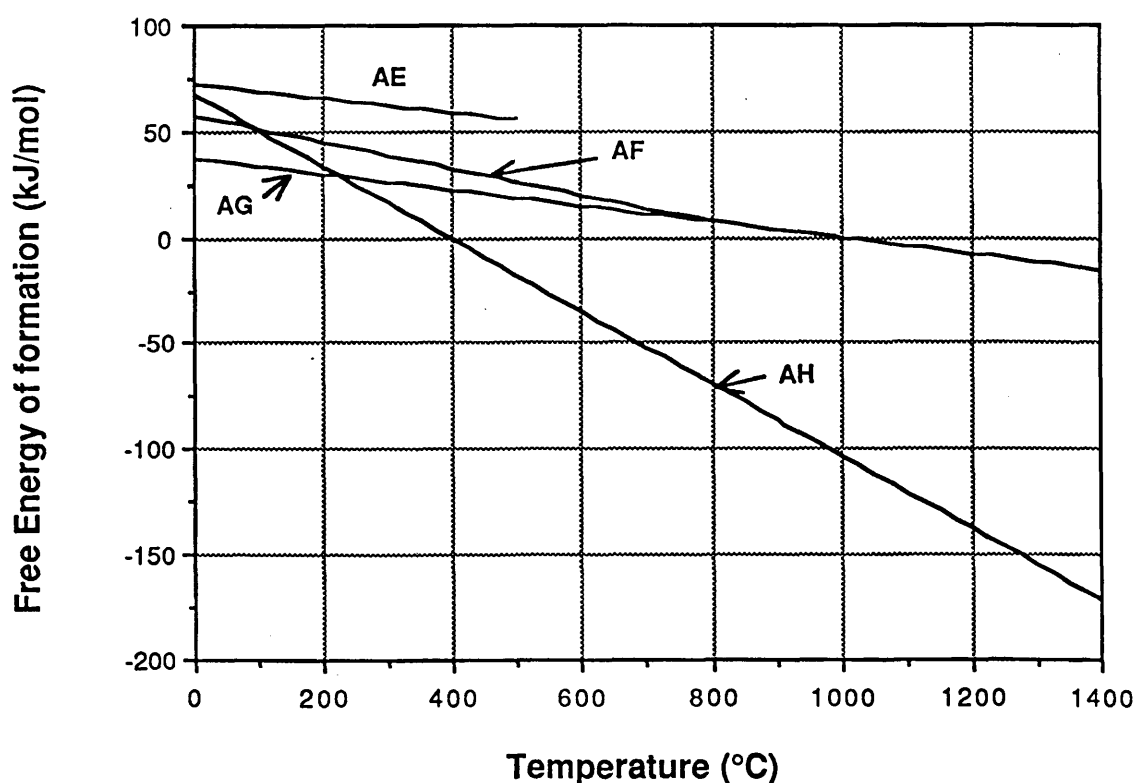


Figure 5.4 Standard free energies of formation for reactions between nickel oxide and sulphides and hydrogen chloride as a function of temperature.

5.2 THE CHLORIDES AND OXYCHLORIDES OF VANADIUM.

No pentachloride of vanadium is known; the apparent non existence of vanadium pentahalides, except VF_5 , has been attributed to steric effects, however, this explanation seems improbable because vanadium (IV) is now known to reach a coordination number of eight with a bidentate arsine. The absence of the pentachloride is more likely to be due to a thermodynamic effect [117].

Two vanadium (V) oxychlorides are known: VOCl_3 and VO_2Cl . VOCl_3 is a yellow liquid which is hydrolysed with extraordinary rapidity in moist air. It is a covalent unsaturated monomer with C_{3v} symmetry [121]. It may be synthesized by reacting dry Cl_2 with the oxides V_2O_3 or V_2O_5 at 600° to 800°C , but temperatures of 300° to 500°C are sufficient in the presence of charcoal or sulphur [117, 121]. It may also be synthesized by passing HCl over V_2O_5 at 150° to 400°C . The thermodynamics of chlorination of V_2O_5 to give VOCl_3 have recently been studied by Sato and Belton [123]. VO_2Cl is a very hygroscopic, orange, crystalline solid which dissolves without decomposition into weakly polar solvents. Cryoscopic measurements indicate that it is a monomer in the vapour state; its structure in the solid state is unknown. It may be prepared by the action of Cl_2O diluted in oxygen into VOCl_3 at room temperature.

Vanadium tetrachloride is a dark reddish-brown liquid which hydrolyses with great rapidity to give solution of the blue VO^{2+} ion [117, 124]. Magnetic and spectroscopic evidence indicate that it consists of unassociated tetrahedral molecules down to its freezing point of -26°C [117, 121, 124]. In the solid form it may exist as a molecular lattice of tetrahedral units [117]. It may be prepared by the action of Cl_2 gas on metallic vanadium, by reaction of CCl_4 on red hot V_2O_5 and by chlorination of ferrovanadium (followed by distillation to separate VCl_4 from Fe_2Cl_6). VCl_4 has a high dissociation pressure and loses chlorine slowly when kept, but rapidly on boiling [117,121].

Vanadium (IV) oxychloride, VOCl_2 , is a green, deliquescent solid, which dissolves in water to give a blue solution. A number of hydrates have been reported but their structures and stoichiometries appear to be in doubt [117]. It can be prepared by reduction of VOCl_3 with zinc powder or hydrogen at 400°C , or by reaction 5.1 below at 600°C [117].



Vanadium trichloride, VCl_3 , is a violet, deliquescent, crystalline solid which readily dissolves in water forming brown solutions of $\text{V}(\text{H}_2\text{O})_6^{3+}$; on addition of aqueous hydrochloric acid the solution turns green, presumably owing to the formation of vanadium (III) chloro-aquo complexes. Its structure is rhombohedral. VCl_3 may be prepared by thermal decomposition of VCl_4 , by reaction of V_2O_3 with thionyl chloride, SOCl_2 , in an autoclave at 200°C for 24 hours, or by reflux of sulphur monochloride, S_2Cl_2 , with V_2O_5 for eight hours [117]. A green, hygroscopic, crystalline hexahydrate is known to exist; it is believed to contain the $[\text{V}(\text{H}_2\text{O})_4\text{Cl}_2]^+$ ion rather than the $\text{V}(\text{H}_2\text{O})_6^{3+}$ ion, on the basis of electronic spectra measurements [117]. VCl_3 disproportionates at high temperatures under an inert atmosphere; if oxygen is present VOCl_3 forms. VCl_3 is believed to vaporize above 650°C [117], but temperatures as low as 450°C have been reported [121].

Vanadium (III) oxychloride, VOCl , is a brown crystalline powder, with an orthorhombic structure. It is not attacked by water, alkalis or hydrochloric acid but dissolves in warm concentrated nitric and sulphuric acids. It is prepared by a chemical transport reaction between VCl_3 and V_2O_3 using a temperature gradient of 620 to 720°C , or by heating VOCl_3 in pure nitrogen. It decomposes above 600°C into VCl_3 and V_2O_3 [117].

VCl_2 is a green, plate-like material, which sublimes without decomposition in an inert or HCl atmosphere above 910°C ; however, in the presence of nitrogen or carbon dioxide the nitride or carbide are formed, respectively. VCl_2 solid is hygroscopic and is soluble in water, alcohol and ether to give purple, blue and green solutions, respectively. It may be prepared by heating VCl_3 for 4 to 6 hours at 475°C in a stream of hydrogen, or by disproportionation of VCl_3 at 800°C in a stream of nitrogen or carbon dioxide. The VCl_4 is carried away by the gas stream leaving VCl_2 behind in the reaction tube.

5.3 FIXED BED VAPOUR TRANSPORT EXPERIMENTS.

Preliminary experiments revealed that vapour transport of vanadium, nickel and iron from Flexicoke was feasible, and factorial design 1 was constructed to investigate the degree of metal extraction and its response to a number of variables. Most authors [122, 125, 126] recommend that in the first factorial experimentation the first design should be highly fractionated and should include a large number of variables. However, as nothing was known about the process, a smaller design with large differences between high and low levels was preferred in order to establish how effective and responsive the process was.

Factorial design 1 was a full 2^3 design with temperature, partial pressure of hydrogen chloride and reaction time as the variables. The chosen responses were the percentages of vanadium, nickel and iron extracted from the coke. The experiments were conducted in a random order to ensure statistical validity of the significance tests. The maximum and minimum levels of the variables are given in Table 5.2. These levels were chosen from the knowledge that for nickel chloride transport to take place high temperatures and high partial pressures of HCl are required. Thus, the minimum and maximum

temperatures selected were 850° and 1100°C, respectively. HCl partial pressures of 1.0 and 0.2 were considered "different" enough to reveal the effect of this variable.

Factor	Variable	Low level	High level	Units measured
A	Temperature	850	1100	°C
B	Partial pressure of HCl	0.2	1.0	-
C	Time	30	180	Minutes

Table 5.2 Variables and their maximum and minimum levels in factorial design 1.

In addition to the chosen variables the following parameters, which may have had an effect on the response, were kept constant during factorial design 1:

- a. Gas Flow rate = 0.75 ml/sec at 20°C.
- b. Coke particle size = As-received Flexicoke.
- c. Mass of coke = 10 g.
- d. Length of coke bed = 10 cm.

Tables 5.3, 5.4 and 5.5 give the experimental design (by means of the treatment codes), extraction results, calculated effects and analysis of variance for vanadium, nickel and iron extractions, respectively. The effects were calculated by the use of Yates' algorithm. The standard deviation of the effects, s_e , was calculated by treating the three-factor interaction, ABC, plus any effects numerically smaller than ABC as being due to experimental error. The value of the three-factor interaction and numerically smaller effects were squared, the squares added and the result divided by the total of their degrees of freedom to give an estimate, s_e^2 , of the variance of

Treatment code	Response % Vanadium extraction	Yates Analysis						Analysis of Variance		
		[1]	[2]	[3]	Divisor	Effect	Factor	Calculated t=Effect/Se	Significance at 99%	Significance at 95%
[1]	1.3	8.5	37.6	114.8	8	14.4	Average	-	-	-
a	7.1	29.2	77.2	25.6	4	6.4	A	6.1	NS	S
b	6.3	26.0	22.4	45.8	4	11.5	B	10.9	S	S
ab	22.9	51.2	3.2	17.5	4	4.4	AB	4.2	NS	NS
c	13.9	5.8	20.7	39.6	4	9.9	C	9.4	NS	S
ac	12.2	16.6	25.1	-19.2	4	-4.8	AC	-4.6	NS	S
bc	23.1	-1.8	10.8	4.4	4	1.1	BC	1.1	NS	NS
abc	28.1	5.0	6.7	-4.1	4	-1.0	ABC	-1.0	NS	NS

Table 5.3 Vanadium extractions, calculated effects and analysis of variance from factorial design 1

Error of effect, Se=1.1%; error of observation, So=1.5%.

(t=9.925 at 99% and 4.303 at 95% probability; 2 degrees of freedom)

S=Significant; NS=non significant.

Treatment code	Response % Nickel extraction	Yates Analysis						Analysis of Variance		
		[1]	[2]	[3]	Divisor	Effect	Factor	Calculated t=Effect/Se	Significance at 99%	Significance at 95%
[1]	0.4	0.9	7.5	48.8	8	6.1	Average	-	-	-
a	0.5	6.6	41.3	10.6	4	2.7	A	1.3	NS	NS
b	1.8	6.1	3.0	37.7	4	8.7	B	4.3	NS	S
ab	4.7	35.2	7.7	16.2	4	4.0	AB	2.0	NS	NS
c	4.5	0.1	5.6	33.7	4	8.4	C	4.2	NS	NS
ac	1.6	2.9	29.1	4.7	4	1.2	AC	0.6	NS	NS
bc	12.3	-2.8	2.9	29.5	4	5.9	BC	2.9	NS	NS
abc	22.8	10.5	13.3	10.5	4	2.6	ABC	1.3	NS	NS

Table 5.4 Nickel extractions, calculated effects and analysis of variance from factorial design 1

Error of effect, $Se=2.0\%$; error of observation, $So=2.9\%$.
 (t=9.925 at 99% and 4.303 at 95% probability; 2 degrees of freedom)
 S=Significant; NS=non significant.

Treatment code	Response % Iron extraction	Yates Analysis						Analysis of Variance		
		[1]	[2]	[3]	Divisor	Effect	Factor	Calculated t=Effect/Se	Significance at 99%	Significance at 95%
[1]	22.7	52.5	125.5	311.1	8	38.9	Average	-	-	-
a	29.8	73.0	185.6	-29.7	4	-7.4	A	-6.2	NS	S
b	30.8	82.7	18.5	40.6	4	10.1	B	8.5	NS	S
ab	42.2	102.8	-48.2	15.3	4	3.8	AB	3.2	NS	NS
c	56.1	7.1	20.5	60.1	4	15.0	C	12.5	S	S
ac	26.6	11.4	20.1	-66.6	4	-16.7	AC	-13.9	S	S
bc	60.7	-29.6	4.3	-0.4	4	0.1	BC	0.1	NS	NS
abc	42.1	-18.6	11.0	6.7	4	1.7	ABC	1.4	NS	NS

Table 5.5 Iron extractions, calculated effects and analysis of variance from factorial design 1

Error of effect, $Se=1.2\%$; error of observation, $So=1.7\%$.

($t=9.925$ at 99% and 4.303 at 95% probability; 2 degrees of freedom)

S=Significant; NS=non significant.

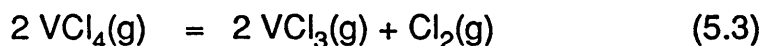
an effect, σ_e^2 . As both negative and positive effects were of interest, the double-sided t-test was applied. The t-test can be used instead of the mean squares and the F-test to examine variances [125] because for a two level factorial design each effect has only one degree of freedom and hence $F=t^2$.

The error of an observation, σ_o , was calculated using the relationship given by equation 5.2 below [125].

$$V(\text{Effect}) = \frac{4}{N} \sigma_o^2 \quad (5.2)$$

where N is the number of observations and $V(\text{effect}) = \sigma_e^2$; when s_e is used as an estimate for σ_e , then equation 5.2 gives s_o as an estimate of σ_o .

The products of the reaction consisted of a purple crystalline solid, together with a brown and a blue-green condensate. The brown condensate was a highly viscous liquid, probably vanadium tetrachloride, VCl_4 , and the blue-green liquid was hydrated VCl_4 . The purple solid gave almost forty diffraction lines, listed in Table 5.6, when analysed by x-ray diffraction, but the identification of these has to date proved impossible. From its general chemistry, colour and the Cl/V ratio, it would appear to be vanadium trichloride, VCl_3 . Vanadium is believed to be present in the coke in the 4+ oxidation state. VCl_3 arises from the thermal decomposition of VCl_4 according to reaction 5.3 below:



Chlorine has been detected in the exit gases. Separate identification of the nickel and iron chlorides has not been possible as these are intimately mixed with the vanadium chloride condensates. In addition to the above products water and H_2S gas were detected during the heating stage, i.e. while the coke bed reached the required temperature; the condensed

water was highly acidic turning universal indicator pH paper red (pH~1). Some sodium has also been found mixed with the metal chlorides.

Tables 5.3, 5.4 and 5.5 show that partial extraction of the metals was achieved and that the different process conditions studied greatly altered the extractions obtained. When the variables were all at their low levels the vanadium and nickel extractions were 1.3% and 0.4% respectively, as compared to extractions of 28% and 23% when all the variables were at their high levels. The extraction of iron was found to be the highest and to be highly responsive to the chosen variables and their level; extractions as high as 61% were obtained.

d spacing (Å)	Relative intensity	d spacing (Å)	Relative intensity	d spacing (Å)	Relative intensity
9.1	W	3.34	W	2.1	MW
7.8	M	3.19	MS	2.15	MW
6.3	M	3.10	MS	2.13	W
5.85	MS	2.97	MW	2.08	W
5.61	MS	2.83	MS	2.02	W
4.89	MW	2.80	W	2.01	W
4.62	M	2.67	MW	1.92	MW
4.35	VS	2.635	M	1.88	W
4.28	W	2.62	W	1.825	W
4.04	S	2.47	MW	1.782	W
3.72	W	2.45	W	1.68	W
3.44	W	2.32	M	1.635	W

Table 5.6 X-ray diffraction data of the crystalline product from the vapour transport experiments.
S=strong; M=medium; W=weak.

For the levels of significance selected it can be seen that variable B (partial pressure of HCl) is the most important variable for the extraction of vanadium. At the 95% confidence level, A (temperature), C (time) and the two-factor interaction AC (time-temperature) are also significant (the most important of these being time). For nickel, no effect is significant at the very stringent 99% confidence level, and only B is significant at the 95% level (it should be noted that the effect for time almost satisfied the 95% confidence level in Table 5.4). For iron, the main effect C and the two-factor interaction AC were significant at the 99% confidence level. At the 95% confidence level, the main effects A and B are also significant. It is interesting to note that the effect for temperature and the temperature-time interaction are negative.

An experiment conducted for 24 hours at 1100°C and with pure HCl produced the following results:

% Vanadium extraction = 42.1%	(28.1%)
% Nickel extraction = 69.5 %	(22.8%)
% Iron extraction = 73.4 %	(42.1%)

The figures in bracket indicate the extractions obtained under similar conditions for a reaction time of three hours, thus, showing that reaction time is a significant variable for the studied reactions.

The above results were reasonably encouraging, and lead to the conclusions that an increase in reaction temperature increases the vanadium extraction, decreases the iron extraction and has little effect on the nickel extraction; in all cases increases in HCl partial pressure and in reaction time increased the extraction of all these metals.

Having established the feasibility of the process, a more comprehensive investigation was undertaken. Factorial design 2 was a $2^{(6-2)}$ fractional factorial design at two levels with the

following six variables: temperature, partial pressures of HCl and water, reaction time, coke particle size and gas flow rate. The variables and their maximum and minimum levels are given in Table 5.7. The measured effects were the vanadium, nickel and iron percentage extractions and the change in the specific surface area of the Flexicoke from the beginning to the end of the reaction. Factorial design 2 was constructed in such a way that variable E= ABC and F=BCD, so that main effects were confounded or aliased with three-factor interactions and higher, and two-factor interactions were aliased with each other. Table 5.8 below gives the confounding pattern for factorial design 2.

In addition to the chosen variables the following parameters, which may have had an effect on the response, were kept constant during factorial design 2:

- a. Mass of coke = 10 g.
- b. Length of coke bed = 10 cm.

Factor	Variable	Low level	High level	Units measured
A	Temperature	900	1100	°C
B	Partial pressure of HCl	0.4	0.9	-
C	Time	60	180	Minutes
D	Partial pressure of water	2.6	15.5	mm Hg
E	Flexicoke particle size	As received	-75 μ m	-
F	Gas flow rate (at 20°C)	0.75	2.0	ml/sec

Table 5.7 Variables and their maximum and minimum levels in factorial design 2.

Full aliased effects	Aliased effects ignoring three factor interactions and higher
<u>Main effects.</u>	
A=BCE=DEF=ABCDF	A
B=ACE=CDF=ABDEF	B
C=ABE=BDF=ACDEF	C
D=BCF=AEF=ABCDE	D
E=ABC=ADF=BCDEF	E
F=ADE=BCD=ABCEF	F
<u>Two-factor interactions.</u>	
AB=CE=ACDF=BDEF	AB=CE
AC=BE=ABDF=CDEF	AC=BE
AD=EF=BCDE=ABCF	AD=EF
AE=BC=DF=ABCDEF	AE=BC=DF
AF=DE=ABCD=BCEF	AF=DE
BD=CE=ACDE=ABEF	BD=CE
BF=CD=ABCE=ABDE=ACEF	BF=CD
<u>Three-factor interactions.</u>	
ABD=CDE=ACF=BEF	
ABF=CEF=ACD=BDE	

Table 5.8 Confounding pattern for factorial design 2.

As for factorial design 1, the Flexicoke was preheated in a nitrogen atmosphere until it reached the required reaction temperature. During preheating a large back pressure was observed on the manometers indicating the release of water, H₂S and organic volatiles; the back pressure was greater with ground coke than with as-received coke. If a flame was placed at the end of the silica tube the emitted fumes burned with a bright smoky yellow flame. The release of volatiles started at around 700°C. DTA/DTG/TG analysis of Flexicoke in nitrogen, Figure 5.5, indicated a small weight loss from room

temperature to 700°C of about 2.4 wt% followed by a larger drop from 700° to 1200°C of 5.2 wt%. The reaction products obtained were the same as in for factorial design 1.

The design layout, metal extractions, calculated effects and analysis of variance are shown in Table 5.9 for vanadium extraction, Table 5.10 for nickel extraction, Tables 5.11 and 5.12 for iron extraction, and Table 5.13 for the change in specific surface area of Flexicoke. Table 5.14 gives the metal extractions from six "centre-point-replicate" runs, in which three runs were performed with the as-received coke and three with -75 μ m ground Flexicoke. The six experiments were carried out in random order after factorial design 2 was completed. From these runs independent estimates of the error of an observation, s_o , were obtained, and using equation 5.2 the error of the effects, s_e , were calculated; these are given in Tables 5.9, 5.10, 5.11 and 5.12. The error of an observation was calculated by finding the variance for each of the three runs with as-received and ground Flexicoke, respectively (each with two degrees of freedom), comparing the two variances by means of an F-test to ensure that they belonged to the same population (with 95% probability), and averaging them to give s_o for a given metal (each with four degrees of freedom). The experimental conditions for the centre point replicate tests were:

Temperature = 1000 °C

Partial pressure of HCl = 0.65.

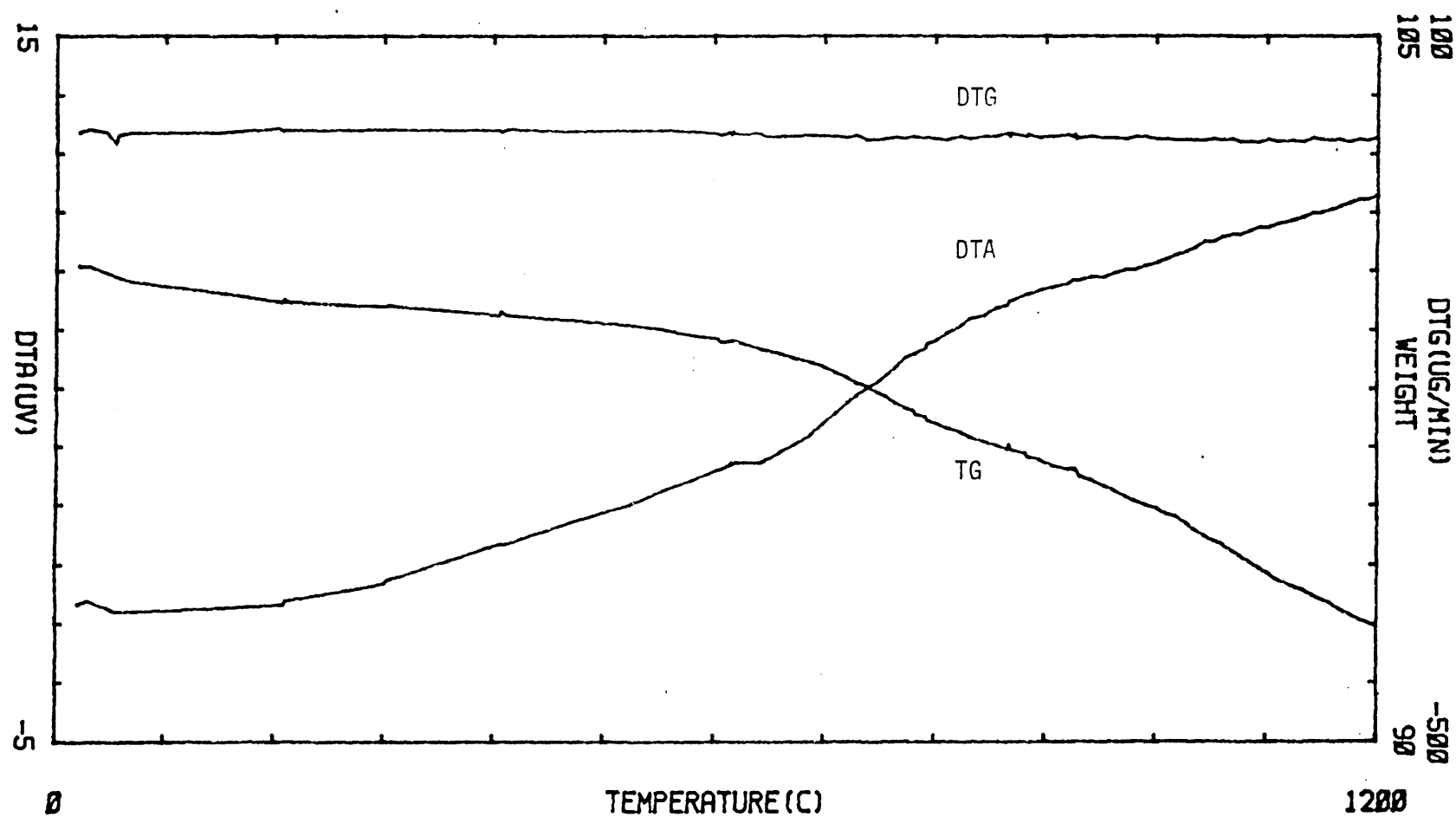
Time = 120 minutes.

Partial pressure of water = 9.1 mm Hg.

Gas flow rate (at 20°C) = 1.37 ml/sec.

The standard deviation of the effects for the change in surface area of Flexicoke was estimated from the three-factor interactions and any effects numerically smaller than these.

Figure 5.5 Thermogravimetric analysis of Flexicoke in a nitrogen atmosphere;
heating rate=5°C/min, mass of coke=51.6mg.



Treatment code	Response % Vanadium extraction	Yates Analysis							Analysis of Variance		
		[1]	[2]	[3]	[4]	Divisor	Effect %	Factor	Calculated t=Effect/Se	Significance at 99%	Significance at 95%
[1]	5.3	39.8	118.1	299.6	541.0	16	33.8	Average	-	-	-
a(e)	34.5	78.3	181.5	241.4	16.3	8	2.0	A	0.7	NS	NS
a(ef)	45.3	99.4	81.8	-23.6	92.1	8	11.5	B	3.9	NS	S
ab(f)	33.0	82.1	159.6	39.9	48.8	8	6.1	AB=CE	2.1	NS	NS
c(ef)	74.7	33.8	16.9	21.3	141.3	8	17.7	C	6.0	S	S
ac(f)	24.7	48.0	-40.5	70.8	10.6	8	1.3	AC=BE	0.4	NS	NS
bc	36.3	51.3	-14.1	17.8	-13.4	8	-1.7	AE=BC=DF	-0.6	NS	NS
abc(e)	45.8	108.1	54.0	31.0	215.8	8	27.0	E	9.2	S	S
d(f)	9.9	29.3	38.5	63.4	-58.2	8	-7.3	D	-2.5	NS	NS
ad(ef)	23.8	-12.3	-17.2	77.9	63.4	8	7.9	AD=EF	2.7	NS	NS
bd(e)	38.0	-50.0	14.2	-57.5	49.6	8	6.2	BD=CF	2.1	NS	NS
abd	10.0	9.5	56.6	68.2	13.1	8	1.6	ABD**	0.5	NS	NS
cd(e)	30.5	13.9	-41.6	-55.7	14.5	8	1.8	BF=CD	0.6	NS	NS
acd	21.1	-28.0	59.4	42.3	125.6	8	15.7	ABF***	5.3	S	S
bcd(f)	22.4	-9.4	-41.9	101.1	98.1	8	12.3	F	4.2	NS	S
abcd(ef)	85.8*	63.4	71.8	114.7	13.7	8	1.7	AF=DE	0.6	NS	NS

Table 5.9 Vanadium extractions, calculated effects and analysis of variance from factorial design 2.

Error of effect, $Se=2.9\%$; error of observation, $So=5.9\%$.

($t=4.604$ at 99% and 2.776 at 95% probability; 4 degrees of freedom)

S=Significant; NS=non significant.

* Average of two runs(79.0 and 92.5%); ** ABD=CDE=ACF=BEF; ***ABF=CEF=ACD=BDE

Treatment code	Response % Nickel extraction	Yates Analysis							Analysis of Variance		
		[1]	[2]	[3]	[4]	Divisor	Effect %	Factor	Calculated t=Effect/Se	Significance at 99%	Significance at 95%
[1]	2.9	6.3	55.2	151.6	250.3	16	15.6	Average	-	-	-
a(e)	3.5	48.9	96.4	98.8	-6.2	8	-0.8	A	-0.9	NS	NS
a(ef)	22.2	52.9	15.3	-7.2	77.6	8	9.7	B	11.7	S	S
ab(f)	26.7	43.5	83.4	1.0	-0.7	8	-0.1	AB=CE	-0.1	NS	NS
c(ef)	25.8	9.1	5.1	33.1	109.3	8	13.7	C	16.5	S	S
ac(f)	27.1	6.3	-12.3	44.6	14.6	8	1.8	AC=BE	2.2	NS	NS
bc	28.6	18.0	-0.9	-11.0	-1.9	8	-0.2	AE=BC=DF	-0.3	NS	NS
abc(e)	14.9	65.4	1.9	10.4	8.3	8	1.0	E	1.3	NS	NS
d(f)	2.7	0.6	42.6	41.2	-52.8	8	-6.6	D	-8.0	S	S
ad(ef)	6.4	4.5	-9.5	68.1	8.2	8	1.0	AD=EF	1.2	NS	NS
bd(e)	5.5	1.3	-2.8	-17.5	11.5	8	1.4	BD=CF	1.7	NS	NS
abd	0.8	-13.7	47.3	2.9	21.4	8	2.7	ABD**	3.2	NS	S
cd(e)	13.2	3.7	4.0	-52.0	26.9	8	3.4	BF=CD	4.1	NS	S
acd	4.8	-4.7	-15.0	50.1	20.3	8	2.5	ABF***	3.1	NS	S
bcd(f)	27.5	-8.4	-8.4	-18.9	102.1	8	12.8	F	15.4	S	S
abcd(ef)	37.9*	10.3	18.8	27.2	46.1	8	5.9	AF=DE	7.1	S	S

Table 5.10 Nickel extractions, calculated effects and analysis of variance from factorial design 2.

Error of effect, Se=0.8%; error of observation, So=1.7%.

(t=4.604 at 99% and 2.776 at 95% probability; 4 degrees of freedom)

S=Significant; NS=non significant.

*Average value of two runs (24.8 and 50.9); ** ABD=CDE=ACF=BEF; ***ABF=CEF=ACD=BDE

Treatment code	Response % Iron extraction	Yates Analysis							Analysis of Variance		
		[1]	[2]	[3]	[4]	Divisor	Effect %	Factor	Calculated t=Effect/Se	Significance at 99%	Significance at 95%
[1]	51.5	95.9	207.2	471.7	850.5	16	53.2	Average	-	-	-
a(e)	44.4	111.3	264.5	378.9	-41.6	8	-5.2	A	-1.6	NS	NS
a(ef)	68.5	123.6	142.5	-51.2	84.7	8	10.6	B	3.3	NS	NS
ab(f)	42.8	140.8	236.3	9.6	130.6	8	16.3	AB=CE	5.1	NS	S
c(ef)	81.4	82.4	-32.8	32.6	151.1	8	18.9	C	5.9	NS	S
ac(f)	42.3	60.1	-18.5	52.1	-18.1	8	-2.3	AC=BE	-0.7	NS	NS
bc	60.1	81.0	21.0	41.2	98.3	8	12.3	AE=BC=DF	3.8	NS	NS
abc(e)	80.7	155.3	-11.4	89.5	190.3	8	23.8	E	7.4	NS	S
d(f)	33.1	-7.1	15.4	57.2	-92.8	8	-11.6	D	-3.6	NS	NS
ad(ef)	49.3	-25.7	17.2	93.8	60.9	8	7.6	AD=EF	2.4	NS	NS
bd(e)	27.6	-39.1	-22.3	14.3	19.5	8	2.4	BD=CF	0.8	NS	NS
abd	32.5	20.6	74.3	-32.4	48.3	8	6.0	ABD**	1.9	NS	NS
cd(e)	68.5	16.1	-18.6	1.7	36.6	8	4.6	BF=CD	1.4	NS	NS
acd	12.5	4.9	59.7	96.6	-46.8	8	-5.9	ABF***	-1.8	NS	NS
bcd(f)	55.3	-56.1	-11.2	78.3	94.9	8	11.9	F	3.7	NS	NS
abcd(ef)	100.0*	44.7	100.7	112.0	33.6	8	4.2	AF=DE	1.3	NS	NS

Table 5.11 Iron extractions, calculated effects and analysis of variance from factorial design 2 (run abcd(ef)=100% Fe extraction).

Error of effect, Se=3.2%; error of observation, So=6.4%.

(t=9.925 at 99% and 4.303 at 95% probability; 2 degrees of freedom)

S=Significant; NS=non significant.

* Measured value 175.6%; ** ABD=CDE=ACF=BEF; ***ABF=CEF=ACD=BDE

Treatment code	Response % Iron extraction	Yates Analysis							Analysis of Variance		
		[1]	[2]	[3]	[4]	Divisor	Effect %	Factor	Calculated t=Effect/Se	Significance at 99%	Significance at 95%
[1]	51.5	95.9	207.2	471.7	840.5	16	52.5	Average	-	-	-
a(e)	44.4	111.3	264.5	368.9	-51.6	8	-6.5	A	-2.0	NS	NS
a(ef)	68.5	123.6	142.5	-51.2	74.7	8	9.3	B	2.9	NS	NS
ab(f)	42.8	140.8	226.3	-0.4	120.6	8	15.1	AB=CE	4.7	NS	S
c(ef)	81.4	82.4	-32.8	32.6	141.1	8	17.6	C	5.5	NS	S
ac(f)	42.3	60.1	-18.5	42.1	-28.1	8	-3.5	AC=BE	-1.1	NS	NS
bc	60.1	81.0	21.0	41.2	88.3	8	11.0	AE=BC=DF	3.4	NS	NS
abc(e)	80.7	145.3	-21.4	79.5	180.3	8	22.5	E	7.0	NS	S
d(f)	33.1	-7.1	15.4	57.2	-102.8	8	-12.9	D	-4.0	NS	NS
ad(ef)	49.3	-25.7	17.2	83.8	50.9	8	6.4	AD=EF	2.0	NS	NS
bd(e)	27.6	-39.1	-22.3	14.3	9.5	8	1.2	BD=CF	0.4	NS	NS
abd	32.5	20.6	64.3	-42.4	38.3	8	4.8	ABD**	1.5	NS	NS
cd(e)	68.5	16.1	-18.6	1.7	26.6	8	3.3	BF=CD	1.0	NS	NS
acd	12.5	4.9	59.7	86.6	-56.8	8	-7.1	ABF***	-2.2	NS	NS
bcd(f)	55.3	-56.1	-11.2	78.3	84.9	8	10.6	F	3.3	NS	NS
abcd(ef)	90.0*	34.7	90.7	102.0	23.6	8	3.0	AF=DE	0.9	NS	NS

Table 5.12 Iron extractions, calculated effects and analysis of variance from factorial design 2 (run abcd(ef)=90% Fe extraction).

Error of effect, Se=3.2%; error of observation, So=6.4%.

(t=9.925 at 99% and 4.303 at 95% probability; 2 degrees of freedom)

S=Significant; NS=non significant.

* Measured value 175.6%; ** ABD=CDE=ACF=BEF; ***ABF=CEF=ACD=BDE

Treatment code	Change in surface area m ² /g	Yates Analysis							Analysis of Variance		
		[1]	[2]	[3]	[4]	Divisor	Effect m ² /g	Factor	Calculated t=Effect/Se	Significance at 99%	Significance at 95%
[1]	-8.8	-1.3	-54.7	-55.1	-24.2	16	-1.5	Average	-	-	-
a(e)	7.5	-53.3	-0.4	30.9	-30.0	8	-3.7	A	-1.9	NS	NS
a(ef)	-23.5	-11.5	25.9	17.8	-22.8	8	-2.9	B	-1.5	NS	NS
ab(f)	-29.9	11.0	5.0	-47.8	-9.7	8	-1.2	AB=CE	-0.6	NS	NS
c(ef)	0.1	11.2	9.9	-29.5	33.3	8	4.2	C	2.2	NS	NS
ac(f)	-11.6	14.7	7.9	6.7	-9.8	8	-1.2	AC=BE	-0.6	NS	NS
bc	-4.3	0.9	-20.0	8.5	74.1	8	9.3	AE=BC=DF	4.8	S	S
abc(e)	15.3	4.1	-27.8	-18.3	30.4	8	3.8	E	2.0	NS	NS
d(f)	11.3	16.3	-52.0	54.2	86.0	8	10.8	D	5.6	S	S
ad(ef)	0.0	-6.4	22.5	-21.0	-65.5	8	-8.2	AD=EF	-4.2	NS	S
bd(e)	11.7	-11.7	3.5	-2.0	36.2	8	4.5	BD=CF	2.3	NS	NS
abd	3.0	19.6	3.2	-7.8	-26.8	8	-3.4	ABD*	-1.7	NS	NS
cd(e)	2.2	-11.3	-22.7	74.4	-75.2	8	-9.4	BF=CD	-4.9	S	S
acd	-1.3	-8.7	31.2	-0.3	-5.8	8	-0.7	ABF**	-0.4	NS	NS
bcd(f)	14.2	-3.5	2.6	53.9	-74.8	8	-9.4	F	-4.8	S	S
abcd(ef)	-10.1	-24.3	-20.9	-23.5	-77.4	8	-9.7	AF=DE	-5.0	S	S

Table 5.13 Change in specific surface area, calculated effects and analysis of variance from factorial design 2.

Error of effect, Se=1.9%; error of observation, So=2.7%.

(t=4.604 at 99% and 2.776 at 95% probability; 4 degrees of freedom)

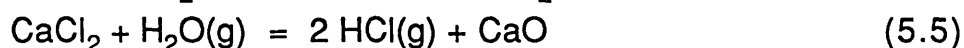
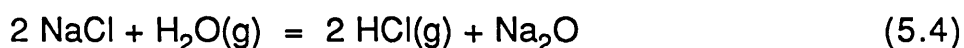
S=Significant; NS=non significant.

Experiment code	% Vanadium extraction	% Nickel extraction	% Iron extraction
CPU	34.8	33.6	51.3
CPU	26.0	29.8	56.8
CPU	28.7	29.5	64.1
CPG	45.1	21.4	190.7
CPG	55.6	21.4	239.9
CPG	58.3	20.4	167.6

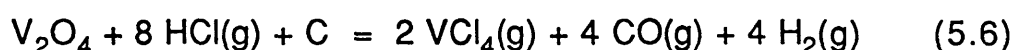
Table 5.14 Metal extractions from centre point replicate tests. CPU=As-received Flexicoke; CPG=-75 μ m ground Flexicoke.

Errors in the iron extractions from ground Flexicoke were found for the abcd(ef) run in factorial design 2 and the centre point replicate tests. The abcd(ef) run was the last to be performed, and the centre point experiments were conducted after the design. The ground coke appeared to be contaminated with a small quantity of iron, giving rise to extractions greater than 100%. The iron extraction from the abcd(ef) run (where all the variables were at their high level) would be expected to be high, and Tables 5.11 and 5.12 were calculated assuming that the iron extractions from this run were 100% and 90%, respectively. These tables show that there is little change in the value of the calculated effects with these two assumed extractions, and the significant effects are the same for both of them. The standard deviation for the iron extraction was taken from the centre point replicates with as-received coke (two degrees of freedom). For vanadium and nickel extractions the variances for the as-received and ground coke were found, with greater than 95% probability, to belong to the same population; thus it is a reasonable assumption that the same also applies for iron extraction.

From Table 5.9 it may be seen that the variables affecting the vanadium extraction at the 99% confidence level were C (time), E (Flexicoke particle size) and the aliased three-factor interaction ABF=CEF=ACD=BDE. At the 95% level, B (partial pressure of HCl) and F (flow rate) are also significant. Clearly the extraction of vanadium is highly dependent on the particle size (as-received Flexicoke has an average particle size of 143 μ m). As found in factorial design 1, the extraction of vanadium is dependent on HCl partial pressure and on reaction time. In addition an increase in flow rate was also found to have a significant effect. Temperature no longer shows a significant effect, probably because of the much higher error level in factorial design 2. This error was independently found, and is thus a better estimate of the experimental error than that used in factorial design 1. It is also worth noting that variable D (H₂O partial pressure) had no effect on the vanadium extraction. Indeed when both factorial designs 1 and 2 are compared the change in vanadium extraction in going from a partial pressure of water of zero to that of 15.5 mm Hg was 1.0 $\pm$ 5.4%. This change can quite safely be ignored. The reason for investigating the effect of water vapour in this process is that in an industrial operation, HCl gas would be formed *in situ* by the high temperature hydrolysis of a chloride salt, i.e.



Although some water vapour would be likely to remain unreacted, the results show that its presence would not affect the vanadium extraction. The remaining water vapour would react with the carbon in Flexicoke producing hydrogen and carbon monoxide gas, which are products in the proposed extraction reaction:



The aliased three-factor interaction ABF=CED=ACD=BDE was found to be statistically significant. It is, however, highly

unlikely that a three-factor interaction will have physical significance, especially as no aliased two-factor interactions are significant at the probability levels chosen (although $AD=EF$ is almost significant at 95% probability). Thus, this interaction is considered to arise from experimental error.

The extractions for vanadium are good, 85% recovery having been achieved, with the most important variables being the particle size, gas flow rate, reaction time and partial pressure of HCl.

The nickel extractions are not so encouraging. Particle size has no effect on extraction, a surprising fact as the nickel distribution in Flexicoke is similar to that of vanadium (Chapter 3). At the 99% confidence limit, the main effects of B (HCl partial pressure), C (time), D (H_2O partial pressure), F (gas flow rate) and the aliased two-factor interaction $AF=DE$ (temperature-flow rate=partial pressure of H_2O -particle size) were found to be significant. At the 95% confidence limit, the aliased two-factor interaction $BF=CD$ (HCl partial pressure-flow rate=time- H_2O partial pressure) and the aliased three-factor interactions $ABD=CDE=ACF=BEF$ and $ABF=CEF=ACD=BDE$ were also found to be significant. Thus, as for vanadium, flow rate, reaction time and HCl partial pressure are important in increasing the nickel extraction. Increases in the water partial pressure have a detrimental effect on nickel extraction. Since at the temperatures used all the moisture is expected to react with carbon, to produce hydrogen and carbon monoxide, it can be inferred that the more reducing the conditions become the lower the nickel recovery. Nickel extraction is, thus, increased by decreasing the boundary layer thickness (i.e. increasing the gas flow rate) and by increasing the reaction time and HCl partial pressure.

Further experiments are required to separate aliased interactions, and it is difficult to explain unambiguously their physical significance. However, $AF=DE$ may arise from the fact

that the flow rate was measured at room temperature, and an increase in reaction temperature will increase the gas velocity due to the increased volumetric expansion of the gas. Interaction $BF=CD$ may arise from the fact that at a given partial pressure of HCl an increase in flow rate will increase the quantity of HCl flowing through the coke bed. Both these aliased two-factor interactions are positive, as expected by the above arguments. Explanation of the aliased three-factor interactions $ABD=CDE=ACF=BEF$ and $ABF=CEF=ACD=BDE$ is not possible without further experimentation and will be assumed to have arisen from experimental error.

From Tables 5.11 and 5.12 it can be seen that for iron extraction no effect was significant at the 99% probability level. At the 95% probability level the main effects C (time) and E (coke particle size) and the aliased two-factor interactions $AB=CE$ (temperature-HCl partial pressure=time-particle size) were found to be significant. The aliased two-factor interaction $AB=CE$ almost certainly arises from CE, since neither the main effects A nor B were significant. The coke particle size and reaction time are seen to be important in increasing the iron extraction from Flexicoke. HCl partial pressure and reaction temperature are not significant in factorial design 2, whilst they were significant for factorial design 1. Tables 5.11 and 5.12 show that as the assumed result for run abcd(ef) increases to its maximum (100%) the effect for HCl partial pressure increases and so, even if the extraction level for this run was over estimated, effect B would not be significant. As the assumed result for run abcd(ef) increases the effect for temperature decreases (becomes less negative), but an unlikely low value for run abcd(ef) would be required to make effect A significant. So it can be quite reasonably assumed that only the main effects C and E and the aliased two-factor interactions $AB=CE$ were significant for iron extraction.

Table 5.13 shows the results for the change in coke surface area as the reaction proceeded. This data is important in two

respects; firstly by increasing the surface area the rate of metal extraction should increase; and secondly it reveals the process parameters which can be altered to produce the desired surface area for the Hall-Heroult anode feed coke. At the 99% probability level the main effects D and F and the aliased two-factor interactions $AE=BC=DF$, $BF=CD$ and $AF=DE$ were found to be significant. Additionally, the aliased two-factor interaction $AD=EF$ was also found to be significant at the 95% probability level. Of all the aliased two-factor interactions, only $AE=BC=DF$ has one interaction which is composed of two significant main effects (D and F); the other interactions are unlikely to be significant and probably arise from an under estimation of the error level.

The specific surface area is seen to increase with increases in the partial pressure of water vapour. Water is expected to react with carbon in Flexicoke forming, probably, small pits and crevices which increase the coke surface area. An increase in flow rate produces a decrease in the coke surface area, even though the water-carbon reaction should be faster (the effect for temperature is not significant, and a diffusion control reaction is assumed) because of the decrease in boundary layer thickness, and at a given partial pressure of water an increase in flow rate increases the quantity of water entering the furnace. Thus, it appears that surface area increases with increasing quantity of water, reaches a maximum and then decreases with more water additions. This effect has been observed in the oxidation of carbon by oxygen [136] and by carbon dioxide [137]; it is thus quite feasible to occur in this case. Unfortunately, the above reasoning is not compatible with the result from the aliased two-factor interaction $AE=BC=DF$, which should be negative if it is assumed to arise from DF. No clear link could be observed between the change in the specific surface area and the metal extraction from the coke. The surface area is probably affected to a large degree in the preheating stage, and effects such as heating rate and dwell time of the volatiles in the coke bed may be more significant than some of the variables studied.

An experiment was performed, with the same conditions as the centre point replicate runs, to investigate how the metal concentration varied at different positions in the coke bed. The bed was divided into ten samples of one centimetre and analysed for residual metal content by XRF; the results are given in Table 5.15 below. The average concentration of vanadium and nickel were 0.59 and 0.11 wt%; these corresponds to extractions of 42% for vanadium and 43% for nickel which are in reasonable agreement with the average expected from the centre point tests. As can be seen from Table 5.15, the extraction from the first section of the bed is very poor, probably because the gas has not reached the required temperature, however at the far end of the bed good vanadium and nickel extractions can be obtained.

Distance (cm)	Vanadium concentration	% Vanadium extraction	Nickel concentration	% Nickel extraction
1	1.18	-	0.21	-
2	0.95	7.8	0.18	10.0
3	0.86	16.5	0.16	20.0
4	0.77	25.2	0.13	35.0
5	0.45	56.3	0.10	50.0
6	0.38	63.1	0.08	60.0
7	0.38	63.1	0.07	65.0
8	0.35	66.0	0.09	55.0
9	0.28	72.8	0.07	65.0
10	0.26	74.8	0.05	75.0

Table 5.15 Metal concentration as a function of distance along coke bed; as-received coke, 1000°C, pHCl=0.65, pH₂O=9.1 mm Hg, time=120 minutes, flow rate=1.37 ml/sec at 20°C.

Acid leaching of a sample of -75µm ground Flexicoke which had undergone the volatilization reaction produced only an extra 1.5% vanadium and 1.8% nickel extraction.

5.4 FLUIDIZED BED VAPOUR TRANSPORT EXPERIMENTS.

The foregoing results indicated that an increase in gas-solid contact, a decrease in boundary layer thickness and better temperature control should enhance metal recovery from Flexicoke. Since the use of a fluidized bed would give the minimum boundary layer thickness for a given gas mixture, in addition to greater solid-gas contact, excellent mixing and temperature control, a laboratory scale fluidized-bed reactor was built and used for further experimental tests. Furthermore, taking coke samples at various times during the vapour transport reaction enabled the kinetics of the process to be investigated. As changes in particle size substantially alter fluidization characteristics (and hence mass transfer between gas and solid), these tests were ran using one particle size range at a time. Results from factorial design 3, in which as-received Flexicoke was used, and other fluidized bed experiments are described below.

Factorial design 3 was a full 2^3 factorial design with temperature, partial pressure of hydrogen chloride and flow rates as the variables. Table 5.16 gives the maximum and minimum levels for the variables. The flow rates are given as a flow rate ratio, defined as the ratio of the gas flow rate to the theoretical minimum fluidization flow rate. The use of this ratio enables direct comparison of fluidization conditions for coke particles of different size ranges. The minimum fluidization flow rate for the as-received Flexicoke was calculated to be 12.4 ml/sec. The gas flow rates used in these experiments were corrected for thermal volumetric expansion. The response for factorial design 3 was the metal extraction rate. For vanadium, the extraction rates were calculated using the pseudo-first order rate equation shown in equation 5.7 below:

$$R_t = R_{\max}[1-\exp(-K_v t)] \quad (5.7)$$

where R_t is the vanadium extraction at time t , $R_{\max}$ is the maximum vanadium extraction for a given experimental condition and K_v is the rate constant for vanadium extraction. Equation 5.7 fitted the data well with regression coefficients greater than 96% found in all cases. The extraction of nickel was approximately linear with time (until equilibrium was achieved). The best slope of these lines, found by fitting a least square line, was taken as the nickel extraction rate. Regression coefficients greater than 90% were found in all cases. The coke samples were analysed by x-ray fluorescence for residual metal content, and thus, the extraction behaviour of iron could not be investigated because its concentration was too low for quantitative analysis.

In addition to the chosen variables the following parameters, which may have had an effect on the response, were kept constant during factorial design 3.

- a. Mass of coke=40 g
- b. Preheating time = 30 minutes.
- c. Particle size of Flexicoke = As-received (-180 μm).
- d. Maximum reaction time = 180 minutes.

Factor	Variable	Low level	High level	Units measured
A	Temperature	900	1000	$^{\circ}\text{C}$
B	Partial pressure of HCl	0.25	1.0	-
C	Flow rate ratio	1.5	3.0	-

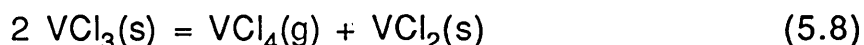
Table 5.16 Variables and their maximum and minimum levels in factorial design 3.

As in the fixed-bed experiments, two main products were obtained from the vapour phase, namely VCl_4 and VCl_3 . The configuration of the fluidized reactor enabled these products to be condensed in different parts of the apparatus. The VCl_3 condensed in the reactor itself, first forming where the temperature was in the $550^\circ\text{-}600^\circ\text{C}$ range. The top part of the reactor and the lid were thus covered with purple crystals. VCl_4 formed in the water condenser and, being liquid, flowed and collected in the bottom of the condenser. The VCl_3 crystals when dissolved in nitric acid gave brown solutions for a few seconds after which they turned green; this effect is characteristic of VCl_3 and has been reported [117] to also occur in hydrochloric acid solutions. The brown colour is claimed to arise from the $\text{V}(\text{H}_2\text{O})_6^{3+}$ complex, and the green solutions from the formation of nitro-aquo (or chloro-aquo) complexes. Solutions of the brown condensates in 1 M nitric acid were blue; the green and blue solutions showed characteristic absorbance peaks for V^{3+} and VO^{2+} , respectively, when analysed by UV spectrophotometry; The nickel and iron chlorides were equally distributed between the two vanadium chloride condensates. In all experiments VCl_4 formed first (usually some three minutes after the start of the reaction). The configuration of the furnace allowed samples of VCl_3 and VCl_4 to be collected and analysed for their Cl/V ratio; the nickel, iron and sodium chlorides were assumed to be in the form of NiCl_2 , FeCl_2 and NaCl , respectively. The Cl/V molar ratios obtained were 3.7 and 3.2 for the brown and purple condensates, respectively, confirming the presence of the proposed VCl_4 and VCl_3 compounds.

In addition, during the preheating stage (i.e. before HCl was passed), H_2S , water and a white waxy solid were obtained; the waxy solid appeared to be formed by the volatile hydrocarbons emitted from the coke.

DTA/DTG/TG analysis of the condensates in a nitrogen atmosphere is shown in Figures 5.6 and 5.7 for VCl_4 and VCl_3 ,

respectively. The VCl_4 , which hydrolysed very rapidly, and was analysed in the form of blue-green liquid, may have nine waters of hydration associated with it; these are released in the temperature range 100° to 220°C , and produce the expected weight loss of 45 wt%. A further weight loss (which is associated with a small exothermic reaction) of about 15 wt% occurs at about 350°C ; this weight loss is equivalent to a loss of about 28 wt% from the dehydrated compound, which is too large for the expected 18 wt% loss for the decomposition of VCl_4 into VCl_3 and Cl_2 . The thermal analysis of the purple crystals showed that two waters of hydration are associated with VCl_3 ; these are released at about 50° and 150°C and produce a loss in weight of about 11 wt%. A further loss in weight of 44 wt% occurs in the temperature range of 500° to 700°C ; the weight loss is equivalent to a 50 wt% weight loss of the dry VCl_3 , which is lower than the 61 wt% loss expected from the disproportionation reaction:



The lower weight loss may be due to the fact that VCl_4 gas will decompose to give solid VCl_3 and Cl_2 gas.

All samples obtained in factorial design 3 were analysed for their Cl/V molar ratio, to investigate how the chosen variables changed the $\text{VCl}_4/\text{VCl}_3$ molar ratio. The results obtained were nonsense since the released water during the preheating stage absorbed HCl gas during the reaction and impossibly large Cl/V ratios were obtained for the bulk solution of metal chlorides.

Figures 5.8 and 5.9 give the extraction versus time curves for vanadium and nickel, respectively, obtained from factorial design 3. Noteworthy from these figures are the large increases in the metal extractions compared to the fixed bed experiments, particularly for nickel. The use of the fluidized bed reactor improved nickel extraction some three times and vanadium extraction twice (for as-received coke reacted for three hours).

Figure 5.6 Thermogravimetric analysis of VCl_4 products in the vapour transport experiments; nitrogen atmosphere, heating rate= $10^\circ\text{C}/\text{min}$, mass of VCl_4 =49.1mg.

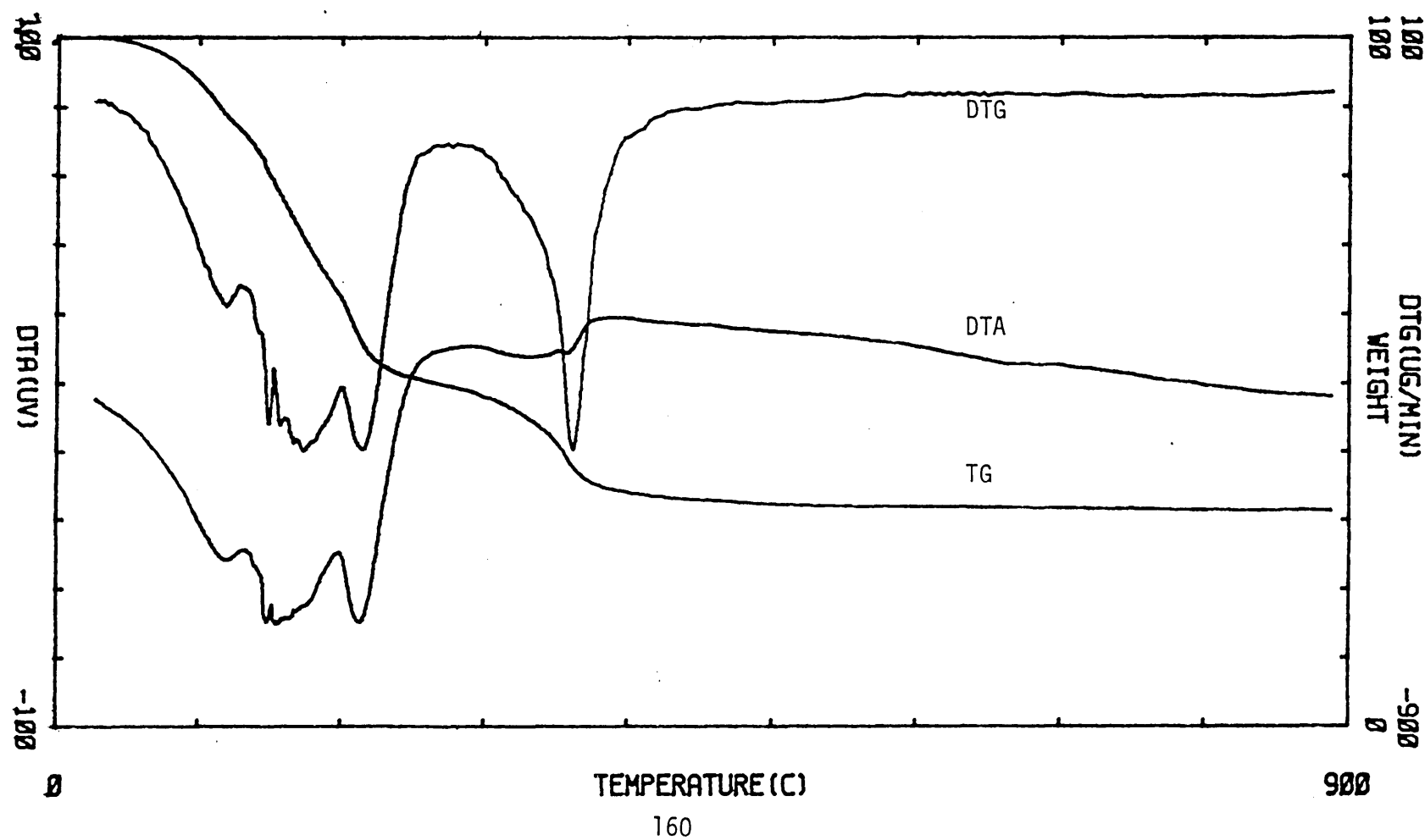
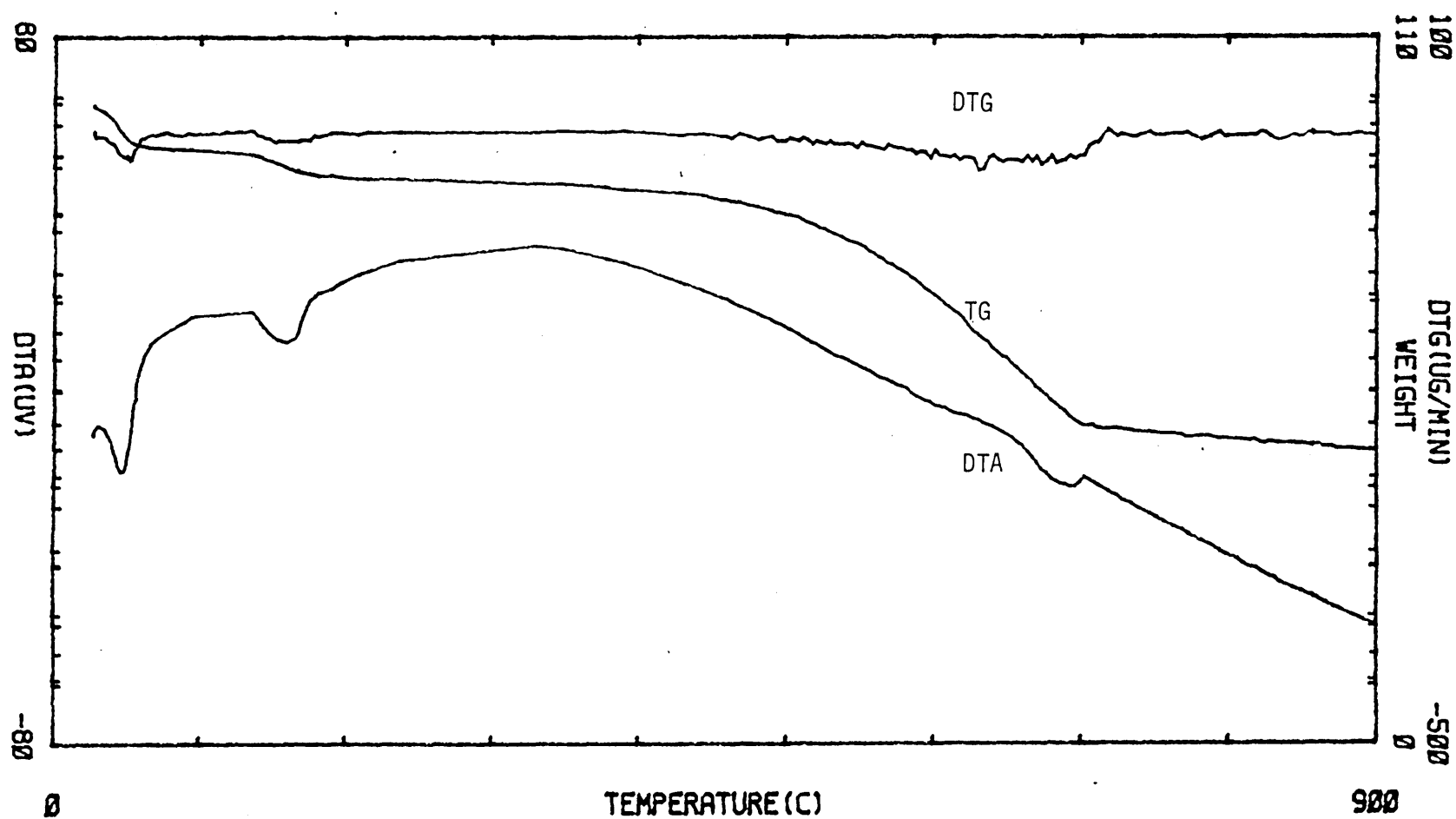


Figure 5.7 Thermogravimetric analysis of VCl_3 products in the vapour transport experiments; nitrogen atmosphere, heating rate= $10^\circ\text{C}/\text{min}$, mass of $\text{VCl}_3=4.1\text{mg}$.



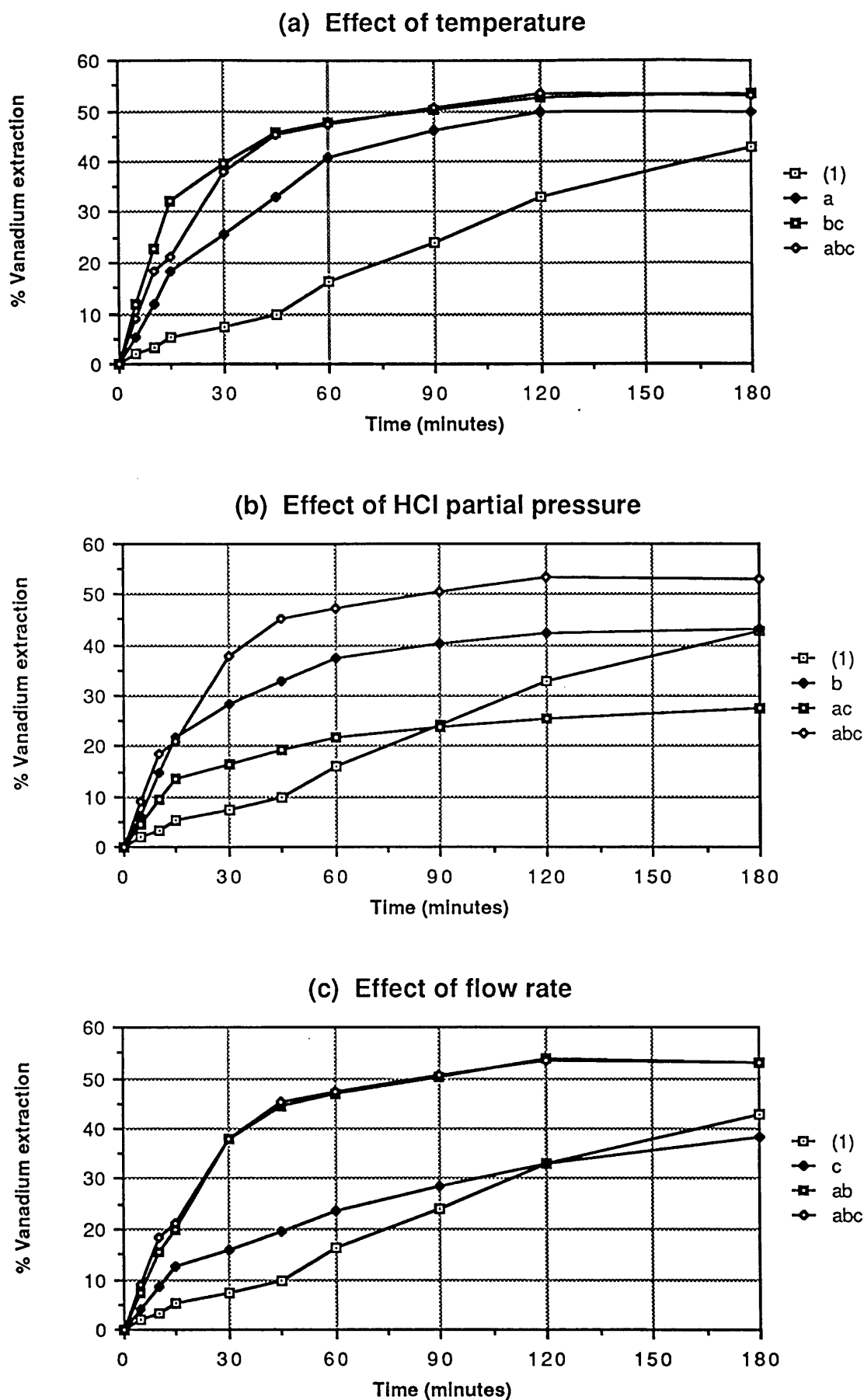


Figure 5.8 Vanadium extraction from factorial design 3

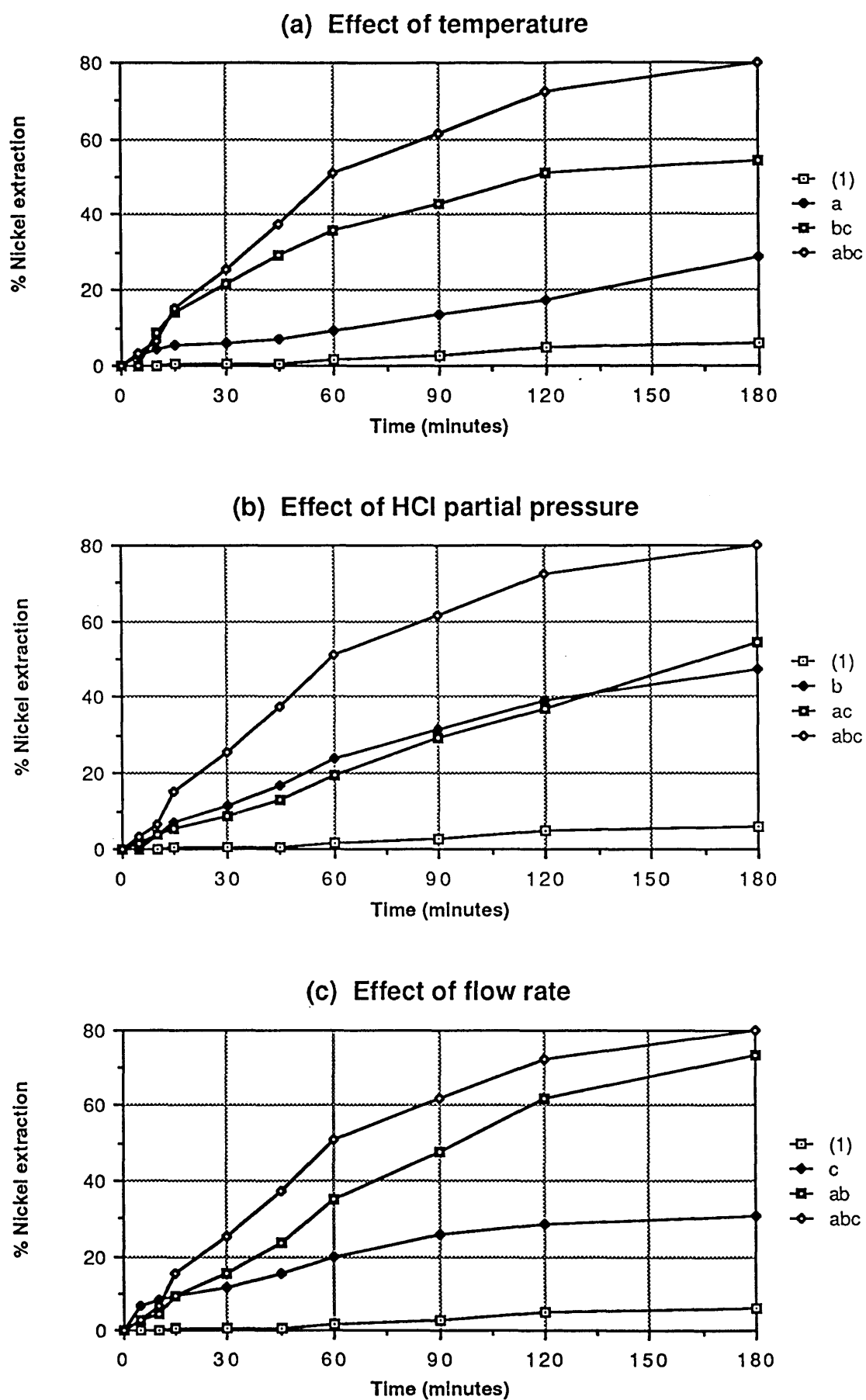
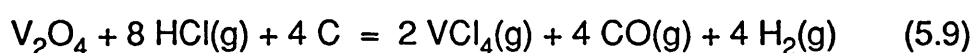


Figure 5.9 Nickel extractions from factorial design 3.

Tables 5.17 and 5.18 give the design layout, calculated response, Yates algorithm and analysis of variance for the vanadium and nickel extraction rates, respectively, for factorial design 3. Experimental errors were calculated in the same manner as factorial design 1. For vanadium, only the main effect of B (HCl partial pressure) is significant at the 99% confidence level. At the 95% confidence level the main effect of A (temperature) and the two-factor interaction AB (temperature-HCl partial pressure) are also significant. Flow rate appeared to have no effect on the vanadium extraction or extraction rate, Figure 5.8 (c). The effect of the two-factor interaction may be seen in Figure 5.8 (a). When variables B and C are at their low level, temperature has a considerable effect on the rate and extent of vanadium extraction, but when they are at their high level, changing the temperature has little effect on the rate and extent of vanadium extraction. Indeed, at the lower partial pressure of HCl, the activation energy for extraction was found to be 82 kJ/mol, whilst at the high HCl partial pressure, the activation energy falls to 4 kJ/mol. Clearly, there is a change from chemical reaction control to diffusion control as the HCl partial pressure is increased, which is shown, with additional data, in Figure 5.10 below. For the proposed extraction reaction:



the rate of diffusion of HCl cannot be rate controlling. If it were, the rate controlling step would be mass transport, and not chemical reaction, at the low HCl partial pressure. Thus, the HCl activity at the reaction interface must be sufficiently high to maintain the equilibrium for reaction 5.9. At the high partial pressure of HCl, the equilibrium at the reaction interface is still maintained, but the quantity of VCl_4 (and CO and H_2) produced is much larger. For chemical reaction control to be maintained the reaction products must be removed at least as fast as they are produced. However, it appears that the rate of product diffusion is not sufficiently high and

Treatment code	Vanadium extraction rate ($\times 10^4/\text{sec}$)	Yates Analysis						Analysis of Variance		
		[1]	[2]	[3]	Divisor	Effect ($\times 10^4/\text{sec}$)	Factor	Calculated $t = \text{Effect}/\text{Se}$	Significance at 99%	Significance at 95%
[1]	1.7	6.3	16.9	35.2	8	4.4	Average	-	-	-
a	4.6	10.6	18.3	4.4	4	1.1	A	3.3	NS	S
b	5.2	6.6	3.1	9.4	4	2.4	B	7.1	S	S
ab	5.4	11.7	1.3	-4.1	4	-1.0	AB	-3.2	NS	S
c	2.7	2.9	4.3	1.4	4	0.4	C	1.1	NS	NS
ac	3.9	0.2	5.1	-1.8	4	-0.5	AC	-1.4	NS	NS
bc	5.8	1.2	-2.7	0.8	4	0.2	BC	0.6	NS	NS
abc	5.9	0.1	-1.1	1.6	4	0.4	ABC	1.2	NS	NS

Table 5.17 Vanadium extractions, calculated effects and analysis of variance from factorial design 3.

Error of effect, $\text{Se} = 3.3 \times 10^{-5}/\text{sec}$; error of observation, $\text{So} = 4.7 \times 10^{-5}/\text{sec}$.
 ($t=5.841$ at 99% and 3.182 at 95% probability; 3 degrees of freedom)
 S=Significant; NS=non significant.

Treatment code	Nickel extraction rate x10 ⁵ /sec	Yates Analysis						Analysis of Variance		
		[1]	[2]	[3]	Divisor	Effect x10 ⁵ /sec	Factor	Calculated t=Effect/Se	Significance at 99%	Significance at 95%
[1]	0.6	3.2	16.1	45.9	8	5.7	Average	-	-	-
a	2.6	12.9	29.8	7.5	4	1.9	A	4.0	NS	S
b	5.1	10.4	4.7	18.7	4	4.7	B	9.9	S	S
ab	7.8	19.4	2.8	3.9	4	1.0	AB	2.1	NS	NS
c	5.3	2.0	9.7	13.7	4	3.4	C	7.3	S	S
ac	5.1	2.7	9.0	-1.9	4	-0.5	AC	-1.0	NS	NS
bc	8.2	-0.2	0.7	-0.7	4	-0.2	BC	-0.4	NS	NS
abc	11.2	3.0	3.2	2.5	4	0.6	ABC	1.3	NS	NS

Table 5.18 Nickel extraction rates, calculated effects and analysis of variance from factorial design 3.

Error of effect, $Se = 4.7 \times 10^{-6}/\text{sec}$; error of observation, $So = 6.6 \times 10^{-6}/\text{sec}$.
 (t=5.841 at 99% and 3.182 at 95% probability; 3 degrees of freedom)
 S=Significant; NS=non significant.

the overall process becomes controlled by the rate of VCl_4 (or CO or H_2) diffusion. The average increase in extraction rate when increasing the HCl gas concentration four-fold would, thus, be expected to be lower than the four times expected from Fick's diffusion law and was indeed found to be only 1.7 times. An alternative mechanism is that the pores become blocked due to the slow diffusion of VCl_4 and the HCl gas is hindered from diffusing to the reaction interface. Thus, the rate of reaction with pure HCl would be similar to that expected with a much lower HCl partial pressure (about 0.4, judging by the 1.7 times increase in extraction rate from the 0.25 HCl partial pressure level).

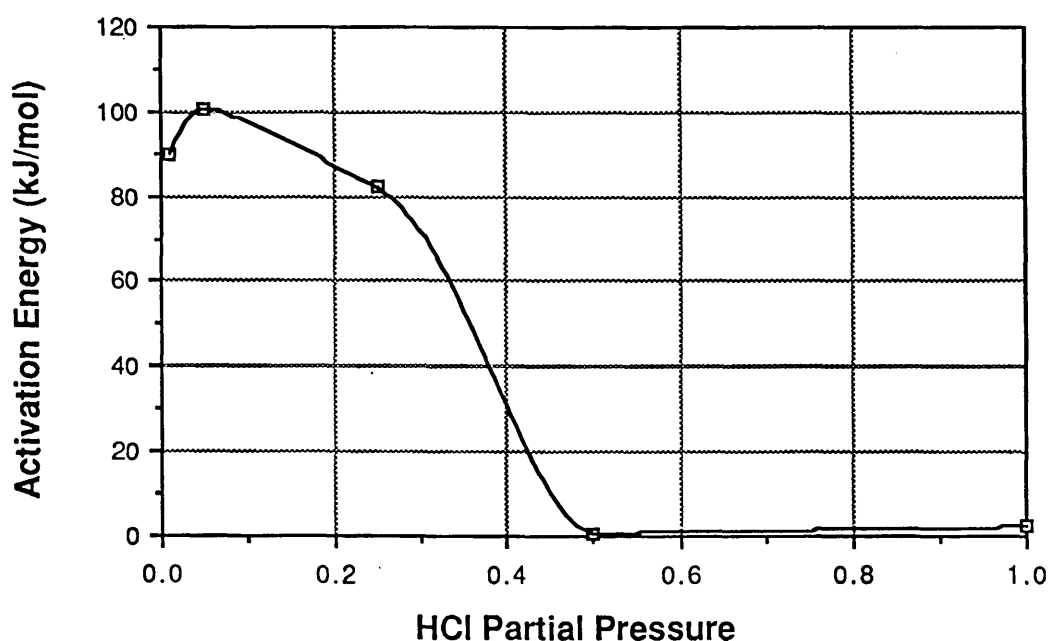


Figure 5.10 Effect of HCl partial pressure on the activation energy for vanadium extraction between 900° and 1000°C ; as-received coke, flow rate ratio=3.0.

Figure 5.10 is only valid in the temperature range 900° to 1000°C . Figure 5.11 below shows an Arrhenius plot for vanadium extraction at two different HCl partial pressures. A change in the rate controlling step of vanadium extraction is seen to occur at 900°C from chemical control to diffusion

control with pure HCl, associated with activation energies of 53 kJ/mol and 4 kJ/mol, respectively. This change does not take place at the lower HCl partial pressure and the reaction remains chemically controlled up to at least 1000°C (with a slightly lower activation energy of 34 kJ/mol).

Figures 5.12 and 5.13 below show the effect of reaction temperature on the vanadium extraction at two HCl partial pressures. The data given in these curves were used to calculate the extraction rates shown in Figure 5.11. Figure 5.12 shows that the extraction curves at 900°, 950° and 1000°C are almost identical, while below 900°C there is a rapid drop in extraction, confirming the change in activation energy shown in Figure 5.11. In Figure 5.13 the vanadium extractions and extraction rates decrease steadily with decreasing temperature, confirming the data shown in Figure 5.11 for 0.25 HCl partial pressure.

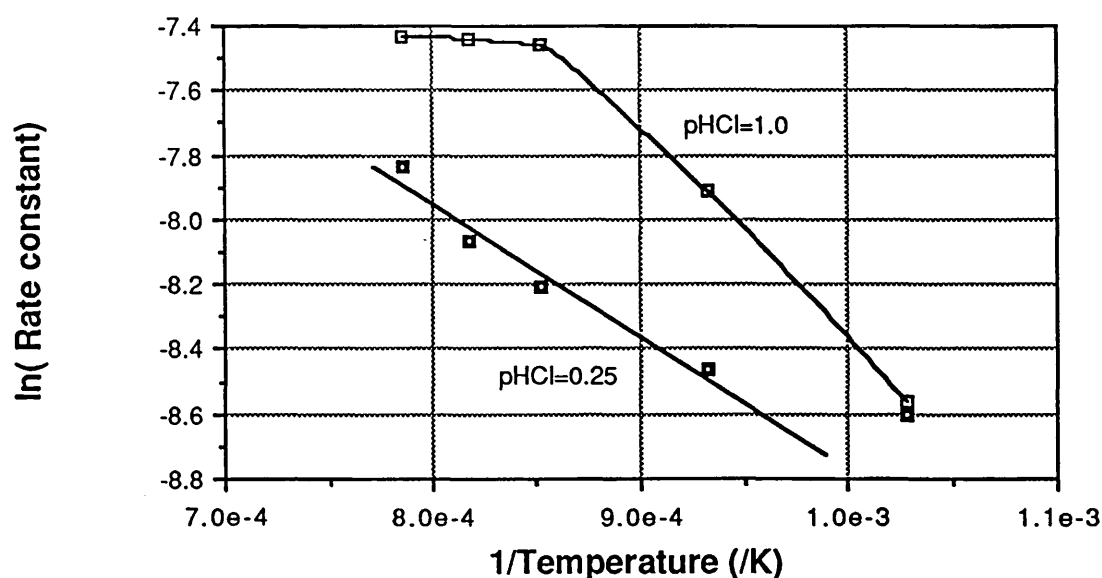


Figure 5.11 Arrhenius plot for vanadium extraction at two different HCl partial pressures from as-received Flexicoke.

The effect of grinding the Flexicoke was to increase both the maximum vanadium extraction (from around 55% to 75-80%) and the extraction rate. Figure 5.14 below shows typical extraction curves for ground Flexicoke and compares them with the extraction from as-received Flexicoke under similar experimental conditions. As already found in factorial design 2, grinding the coke has a large effect on the extraction of vanadium. The three size fractions of ground Flexicoke investigated (namely $-106+90\mu\text{m}$, $-90+75\mu\text{m}$ and $-75+53\mu\text{m}$) showed almost identical vanadium extraction curves. This is indicative that the extraction reaction is chemically controlled, and thus smaller particle size has no effect on the extraction rate. This has been confirmed from estimates (only two temperatures used) of the activation energy of extraction from $-75+53\mu\text{m}$ ground Flexicoke, which were 72 kJ/mol and 68 kJ/mol at HCl partial pressures of 1.0 and 0.25, respectively, between 900° and 1000°C.

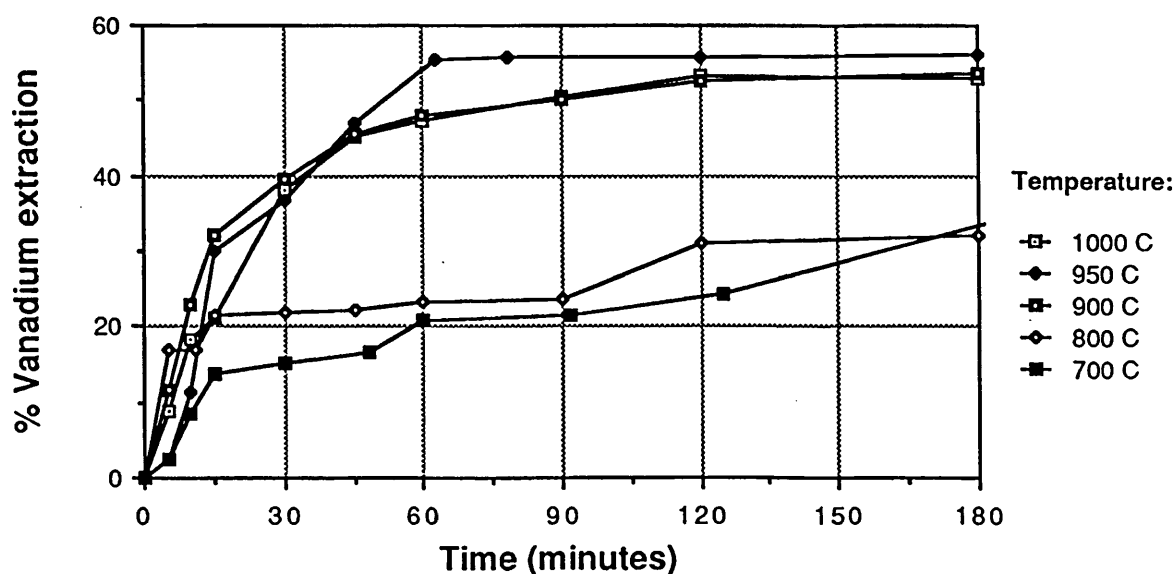


Figure 5.12 Effect of temperature on the vanadium extraction from as-received Flexicoke with pure HCl; flow rate ratio=3.0.

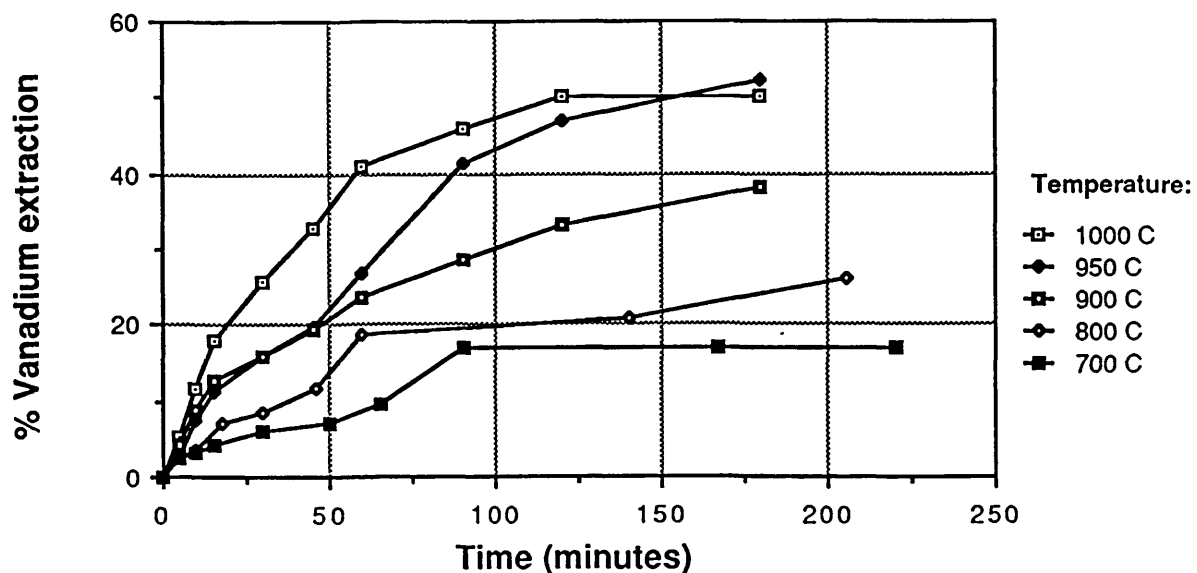


Figure 5.13 Effect of temperature on the vanadium extraction from as-received Flexicoke at a HCl partial pressure of 0.25; flow rate ratio=3.0.

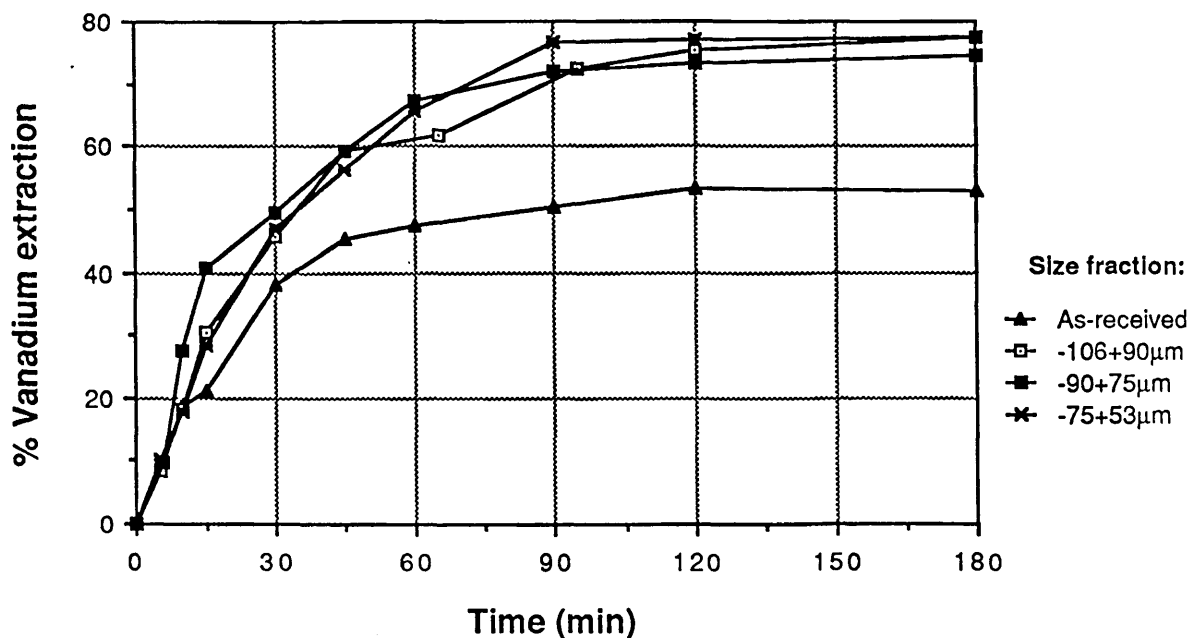


Figure 5.14 Effect of particle size on the vanadium extraction from Flexicoke. Temperature=1000°C; pHCl=1.0; flow rate ratio=3.0.

The actual vanadium extraction rate, as measured by the pseudo-first order rate equation, drops slightly when comparing the ground coke (-106+90 μ m size fraction) to the as-received coke (from 5.9×10^{-4} to 4.9×10^{-4} /sec). Figure 5.14 shows this result to be nonsense, and is due to the mathematical form of the pseudo-first order rate model, equation 5.7; the fraction $R_t/R_{\max}$ does not increase at the same rate as $R_{\max}$ when the coke is ground, and hence the slope (i.e. the extraction rate) appears smaller. Thus, no direct comparison of rates between different size fractions is possible.

A further difficulty in studying the extraction behaviour of ground Flexicoke was the relatively large quantity of coke that was lost from the furnace due to elutriation. The elutriation took place mainly during preheating (due to the increase in gas velocity as the temperature increased and the release of volatiles), but even when equilibrium had been reached and no more fines were released, the introduction of HCl produced another loss of carbon particles. No pressure drop was observed in the manometers associated with this apparent increase in gas velocity. On no occasion was coke elutriated with as-received Flexicoke.

Both ground (-90+75 μ m size fraction) and as-received Flexicoke were used to investigate the effect of HCl partial pressure on the rate of vanadium extraction. Figures 5.15 and 5.16 below show the vanadium extraction curves at 1000°C with different HCl partial pressures for as-received and ground coke, respectively.

As already mentioned, there is a change in the rate controlling step from chemical to diffusion control, which is dependent on the reaction temperature, the HCl partial pressure and the coke particle size. Investigations of the effect of HCl partial pressure on the vanadium extraction from ground coke (because

it is chemically controlled) gave the order of the chemical reaction with respect to HCl concentration.

Figure 5.17 gives a plot of the vanadium extraction rate versus the HCl partial pressure; a linear relationship was obtained from the experiments with ground Flexicoke indicating that the chemical reaction is first order with respect to HCl partial pressure. On the other hand, if as-received coke is used then a curve is obtained due to the change in the rate controlling step from chemical to diffusion control as the HCl partial pressure is increased. The values in Figure 5.17 are not directly comparable between the two curves (due to the mathematical form of the pseudo-first order rate equation). At a given HCl partial pressure the vanadium extraction and extraction rate were always higher for the ground coke.

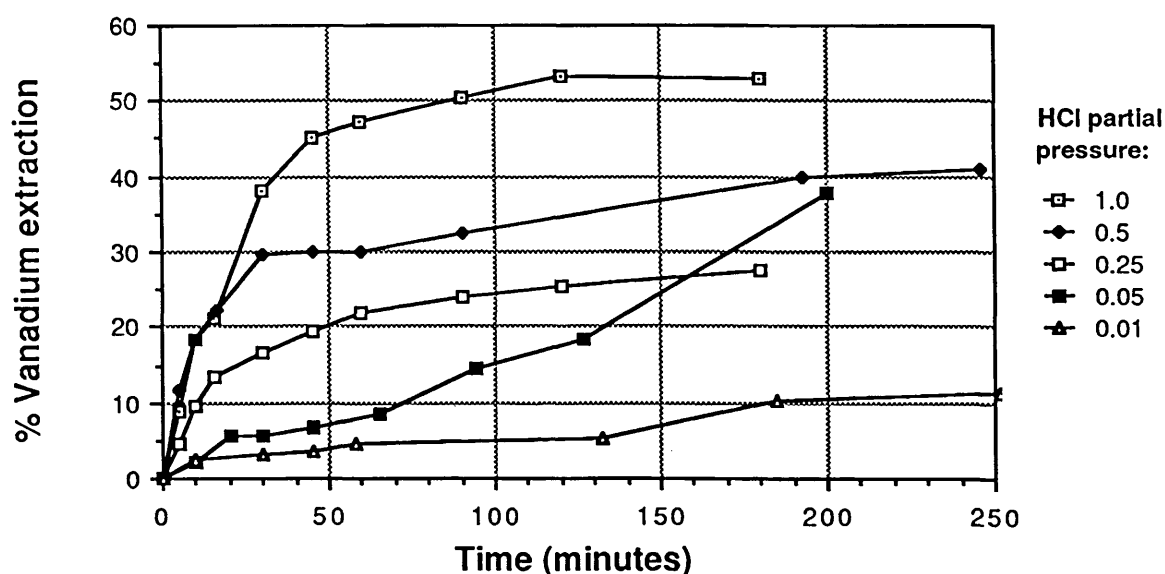


Figure 5.15 Effect of HCl partial pressure on the vanadium extraction from as-received Flexicoke; flow rate ratio=3.0; temperature=1000°C.

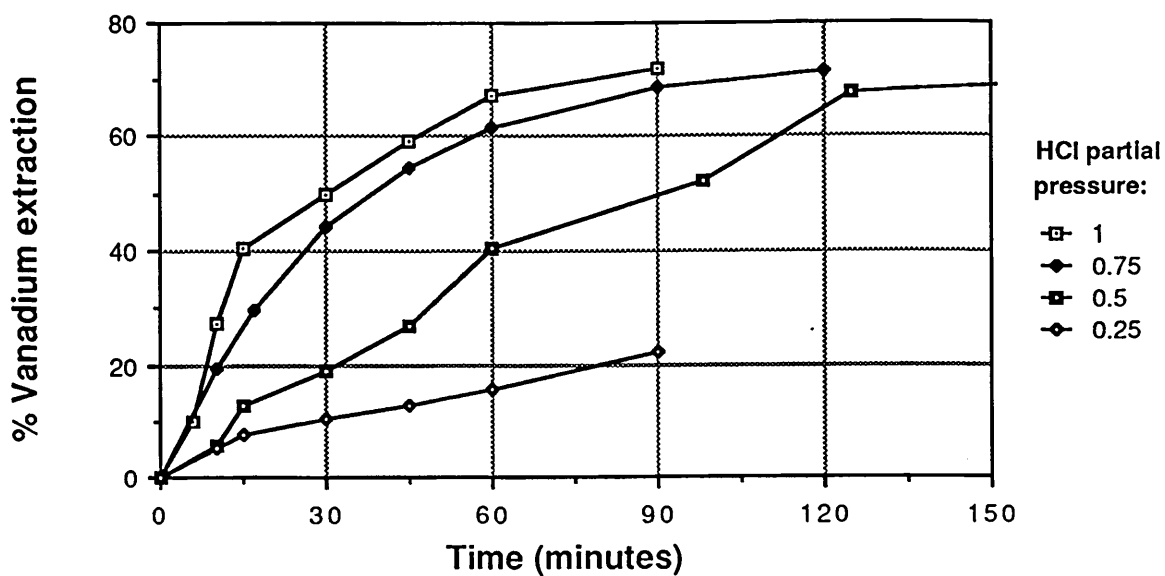


Figure 5.16 Effect of HCl partial pressure on the vanadium extraction from -90+75 μ m ground Flexicoke; flow rate ratio=3.0; temperature=1000°C.

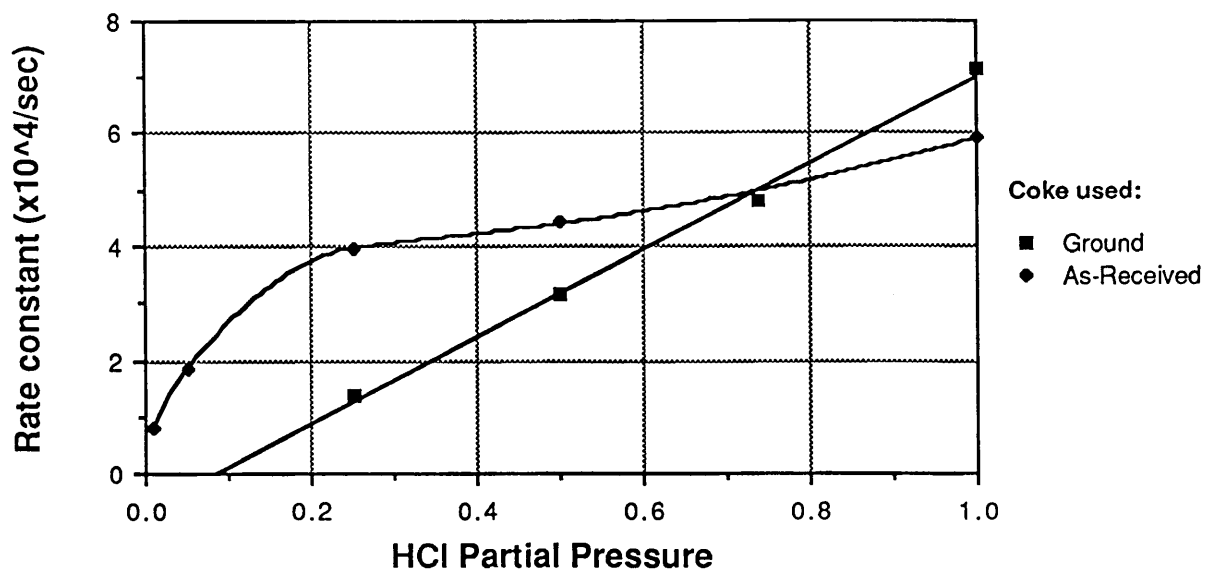


Figure 5.17 Effect of HCl partial pressure on the vanadium extraction rate from as-received and -90 +75 μ m ground Flexicoke; temperature=1000°C, flow rate ratio=3.0.

The rate of nickel extraction was influenced by the main variables A (temperature), B (HCl partial pressure) and C (flow rate). No two-factor interactions were significant at the selected confidence levels. The effect of temperature on the nickel extraction at two different HCl partial pressures is given in Figures 5.18 and 5.19 below. As can be seen from these figures the nickel extraction and extraction rate decreases steadily with decreasing temperature, with no sharp drops being evident in these plots.

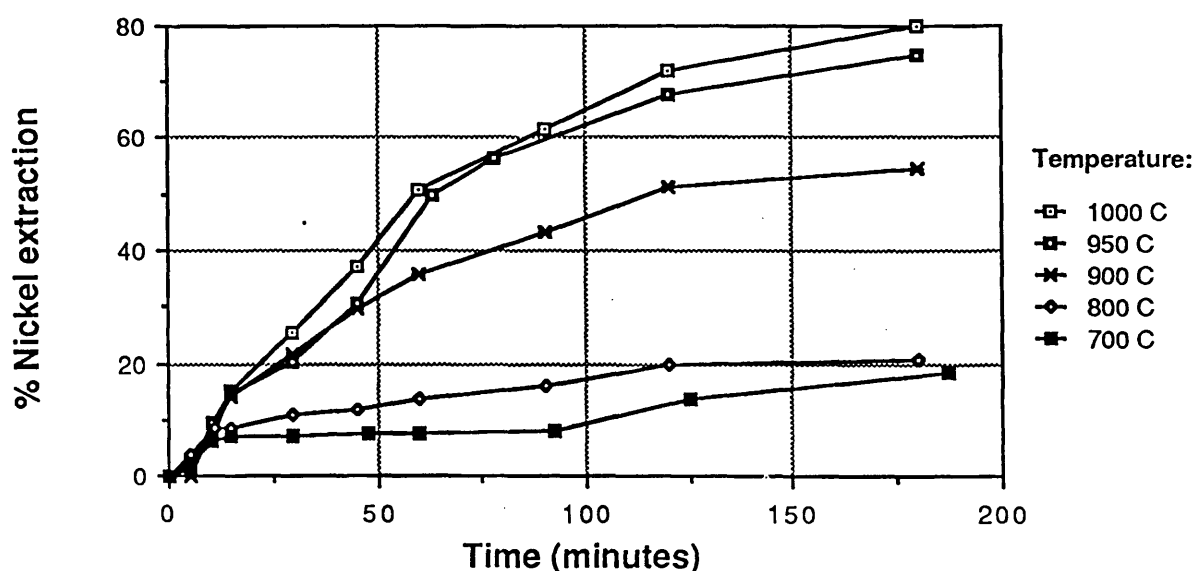


Figure 5.18 Effect of temperature on the nickel extraction from as-received Flexicoke with pure HCl; flow rate ratio=3.0.

The effect of temperature on the nickel extraction rate is given in Figure 5.20 below; straight lines were obtained for the Arrhenius plots at HCl partial pressures of 1.0 and 0.25, giving activation energies of 69 kJ/mol and 60 kJ/mol, respectively, in the temperature range 700° to 1000°C. These results indicate that nickel extraction from Flexicoke is chemically controlled at all HCl partial pressures studied (0.01 to 1.0).

Figures 5.21 and 5.22 show the effect of the HCl partial pressure on the nickel extraction from as-received and ground Flexicoke, respectively, at 1000°C and with a flow rate ratio of 3.0. These figures clearly show that the HCl partial pressure has a large effect on the nickel extraction and extraction rate.

Figure 5.23 below shows the effect of HCl partial pressure on the nickel extraction rate from as-received and ground (-90 +75 μ m) Flexicoke. As can be seen from this figure the extraction of nickel is first order with respect to HCl partial pressure.

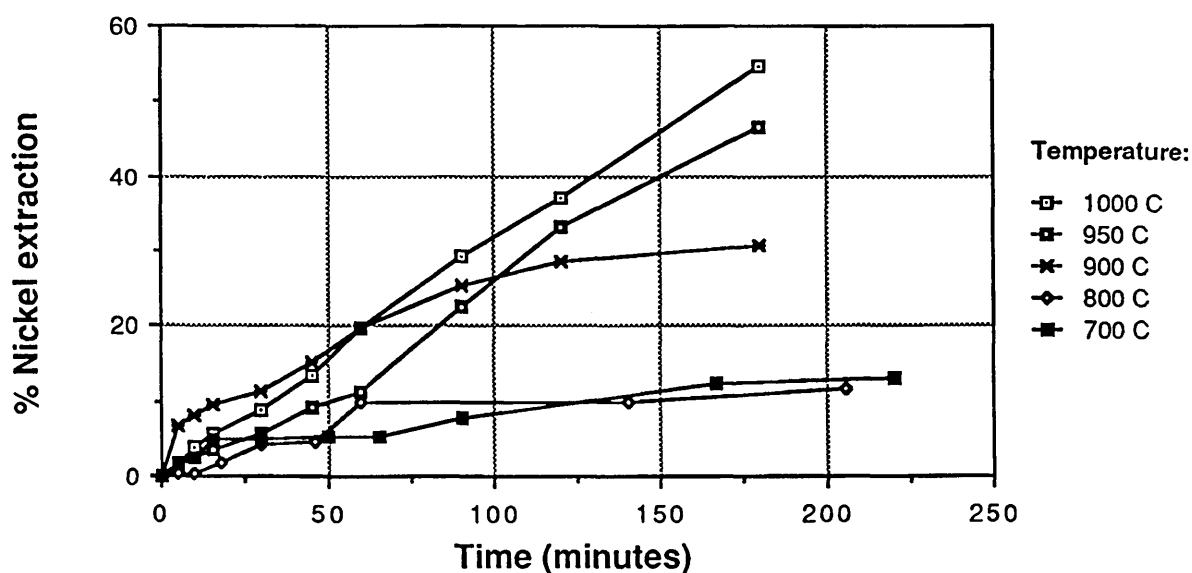


Figure 5.19 Effect of temperature on the nickel extraction from as-received Flexicoke with HCl partial pressure of 0.25; flow rate ratio=3.0.

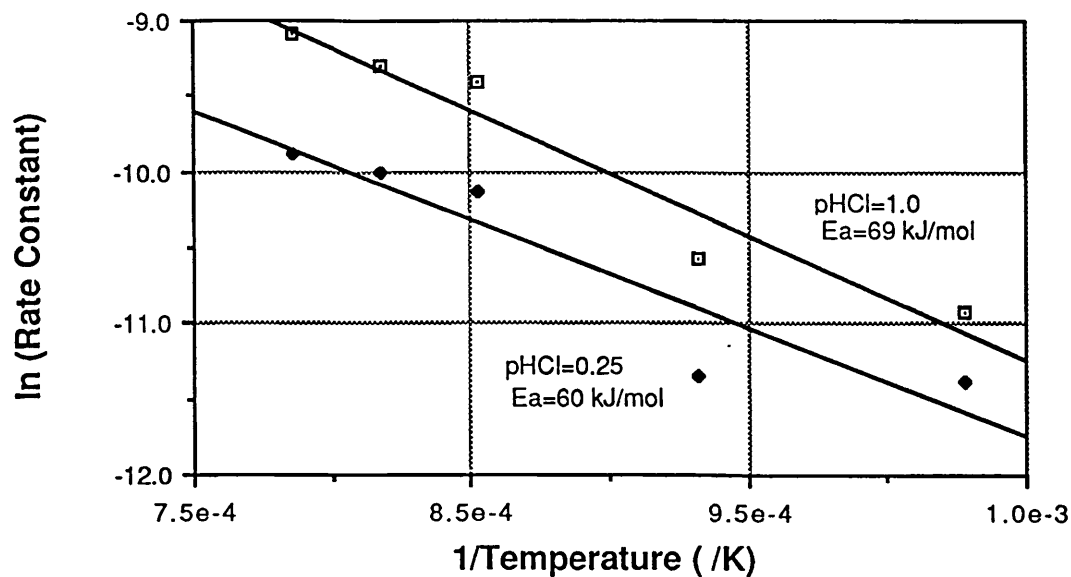


Figure 5.20 Arrhenius plot for nickel extraction at two HCl partial pressures; as-received coke, flow rate ratio=3.0.

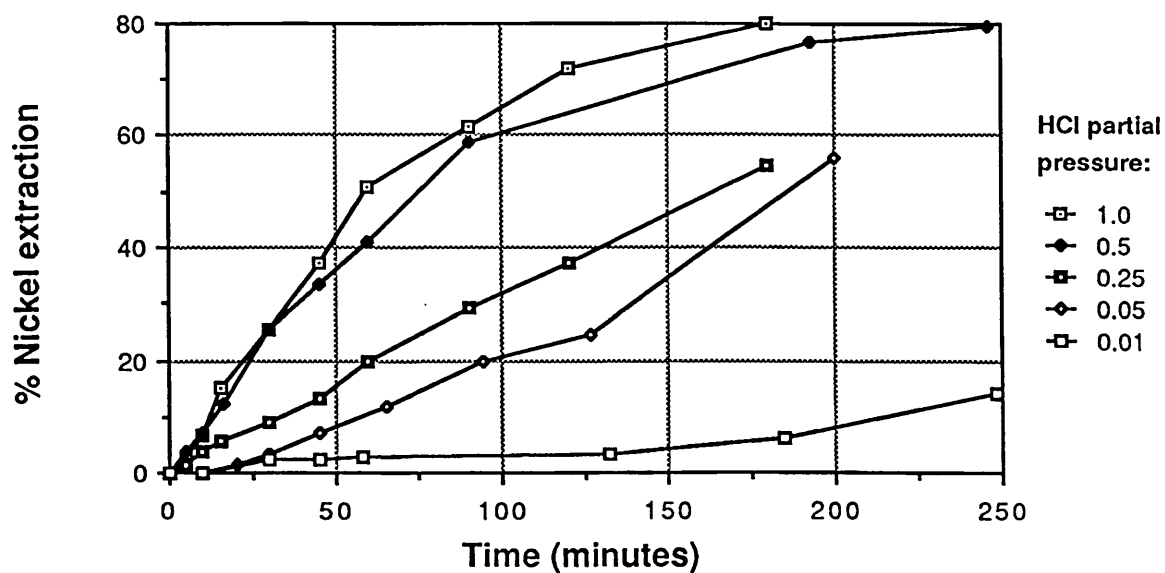


Figure 5.21 Effect of HCl partial pressure on the nickel extraction from as-received Flexicoke; temperature=1000°C, flow rate ratio=3.0.

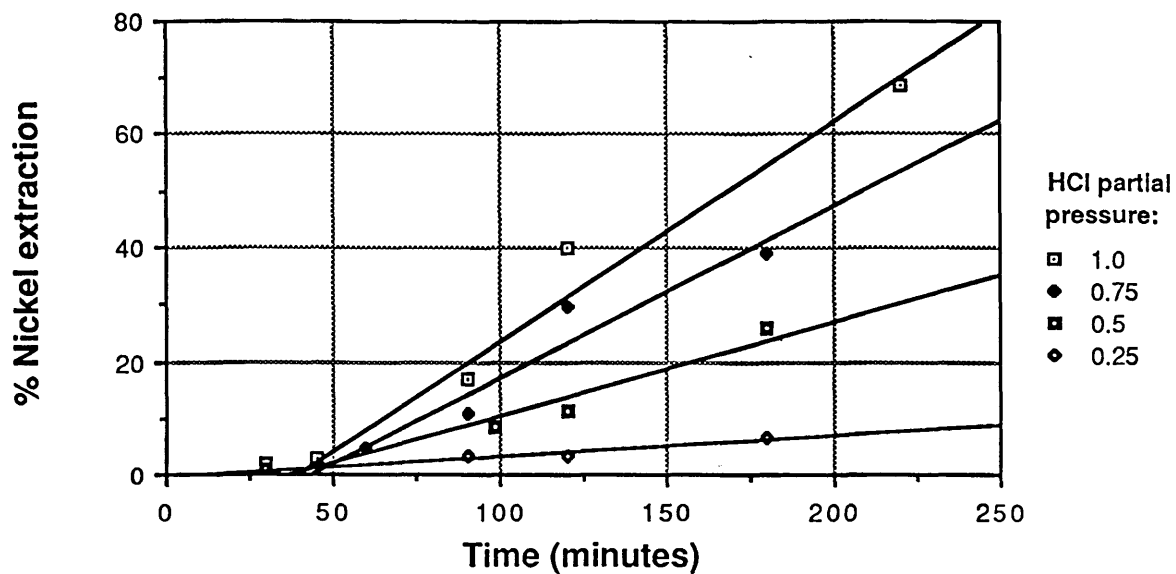


Figure 5.22 Effect of HCl partial pressure on the nickel extraction from -90+75 μ m ground Flexicoke; temperature=1000°C, flow rate ratio=3.0.

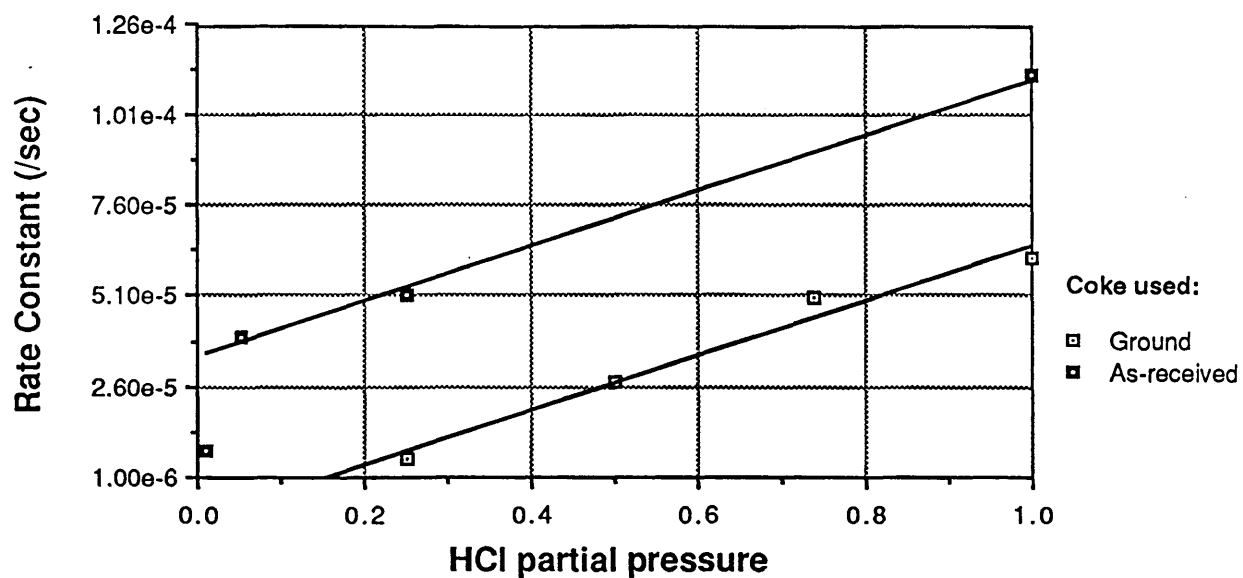


Figure 5.23 Effect of HCl partial pressure on the rate of nickel extraction from as-received and ground Flexicoke; temperature=1000°C; flow rate ratio=3.0; -90 +75 μ m.

Figure 5.23 shows that the rate of extraction from ground Flexicoke is lower than that from as-received Flexicoke at all HCl partial pressures investigated (0.01 to 0.1). This effect appears to be associated with the decrease in gas flow rate (necessary in order to keep the flow rate ratio constant). The effect of flow rate on nickel extraction and extraction rate is as yet not clearly understood. Above a gas flow rate of 8.5 ml/sec (at 20°C) there is no effect; but below this value the elapsed time before which nickel starts to be extracted increases rapidly. Thus, an "induction" time is obtained as shown in Figure 5.24 below. Using the two-phase model for fluidization [129, 130] HCl concentration profiles in the bed have been calculated for both the emulsion and the bubble phase, and no local HCl depletion was indicated for any of the flow rates considered. Appendix B shows details of the calculations. Once the extraction of nickel started, the rate of reaction appeared not to be affected by the flow rate, as shown in Figure 5.25 below. An effect is seen in Table 5.18 because the rates were measured from time zero in all cases.

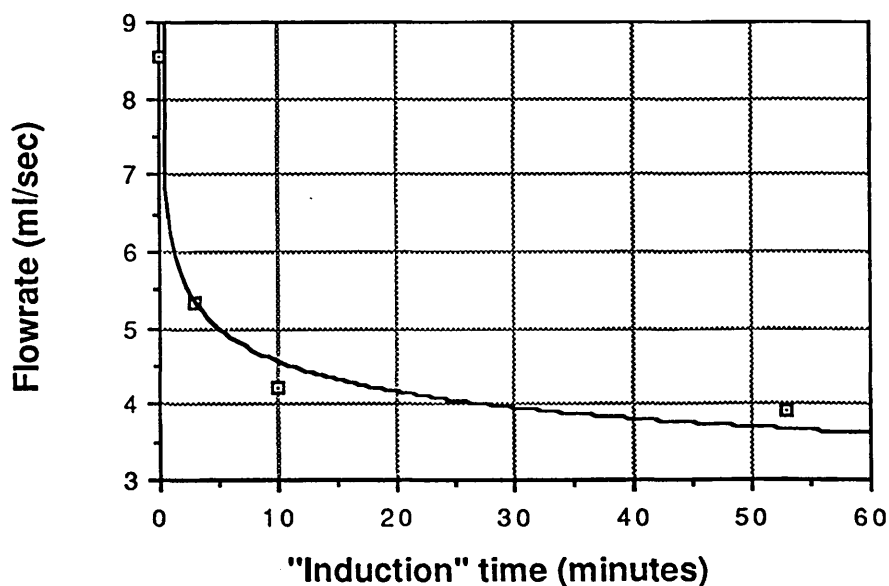


Figure 5.24 Effect of flow rate on the induction time for nickel extraction; temperature=1000°C, as-received coke, HCl partial pressure=1.0.

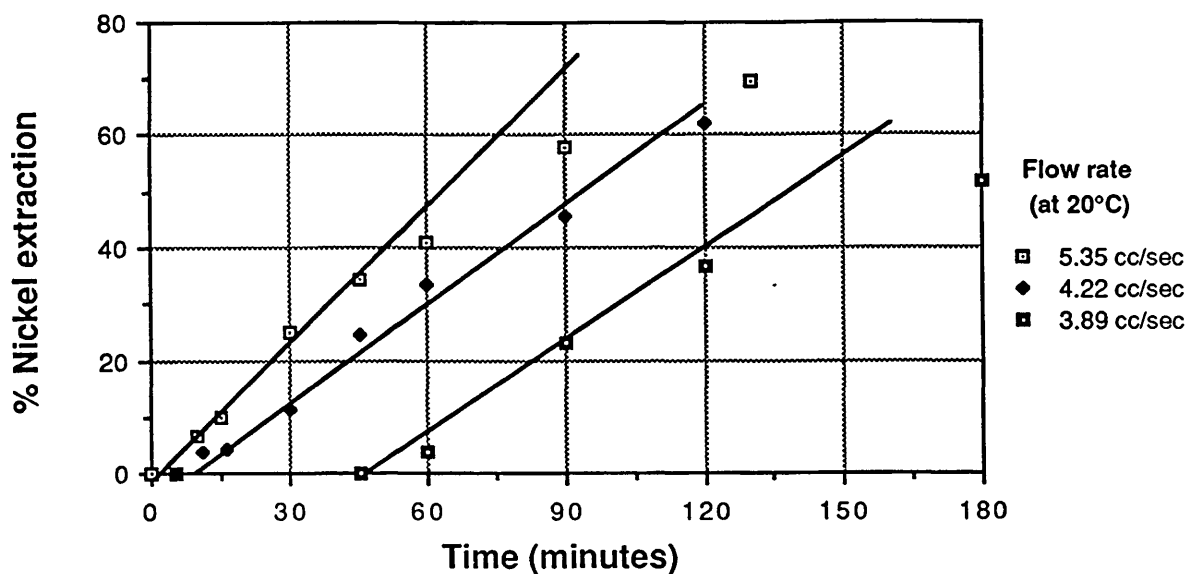


Figure 5.25 Effect of flow rate on the nickel extraction from as-received Flexicoke; HCl partial pressure=1.0, temperature=1000°C.

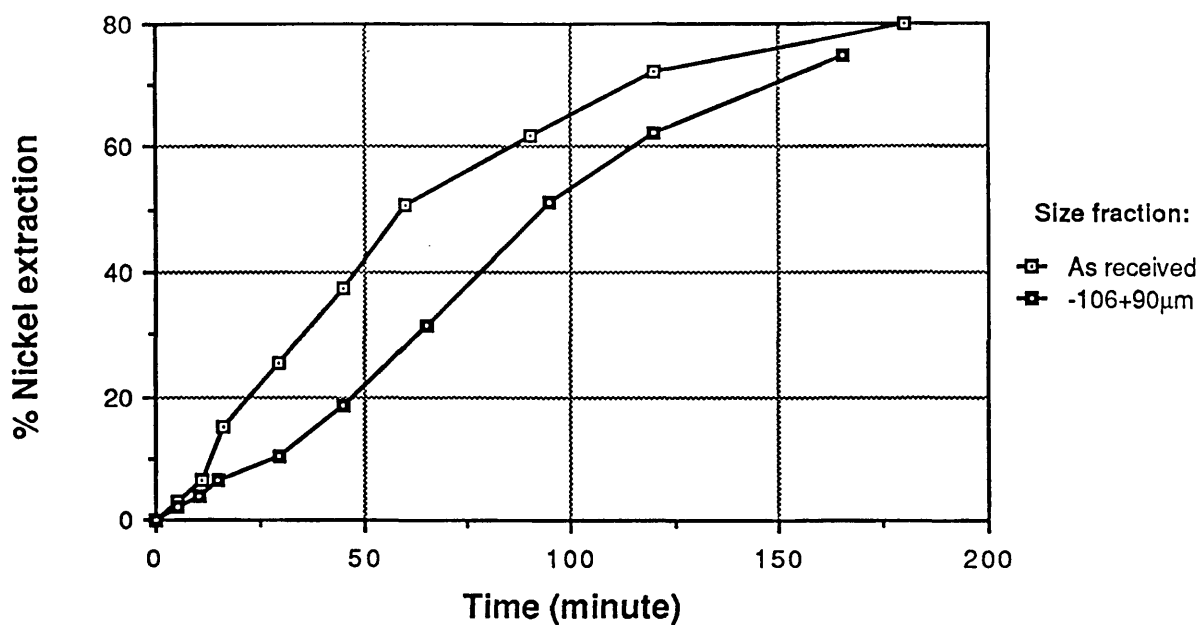


Figure 5.26 Effect of coke particle size on the nickel extraction from Flexicoke; temperature=1000°C, HCl partial pressure=1.0.

The effect of particle size on the metal extractions is shown in Figure 5.26. The lower nickel extraction rate with decreasing particle size (which changes from 11.2×10^{-5} to 7.9×10^{-5} /sec) is probably due to the lower gas flow rate used for fluidization (in order to maintain a constant flow rate ratio). Smaller particle size fractions show even lower extraction and extraction rates.

The heating up process and vapour transport reactions produced some structural changes in the coke. The specific surface area of -150+125 μ m as-received Flexicoke was observed to increase from 3.8 m²/g to 7.2 m²/g as the coke was heated from 25°C to 1000°C in a N₂ atmosphere for 30 minutes. At the end of this period pure HCl gas was introduced into the furnace and the surface area decreased to about 6.35 m²/g in about 30 minutes and remained at that level for the rest of the reaction time, as shown in Figure 5.27. The change in surface area was not reflected by a change in porosity; samples of as-received, zero time (i.e. 30 minutes preheated) and 90 minutes reacted coke showed negligible porosity in the pore diameter range 0.1 to 30 μ m (examination below 0.1 μ m resulted in particle compression leading to false results) when examined by mercury porosimetry.

Samples of -150+125 μ m as-received Flexicoke were also analysed with the electron microprobe to investigate the concentration of vanadium, nickel and sulphur as a function of radial distance in a particle. Analyses were performed for samples collected at zero reaction time and after 90 minutes of reaction; the analysis was conducted by placing the electron beam at the edge of the particle and analysing along a diameter every 2 μ m. The operation was repeated with eight diameters for each time sample. Analysed particles were chosen at random, but only spherical particle with diameters of about 140 μ m were investigated, to ensure that the analysis was conducted through the centre of the particle. The vanadium, nickel and sulphur distributions at zero time and the vanadium

and sulphur distributions at 90 minutes are given in Figure 5.28 to 5.31 below, and Plate 5.1 and 5.2. The distribution of nickel after 90 minutes could not be investigated because its concentration was too low for qualitative analysis.

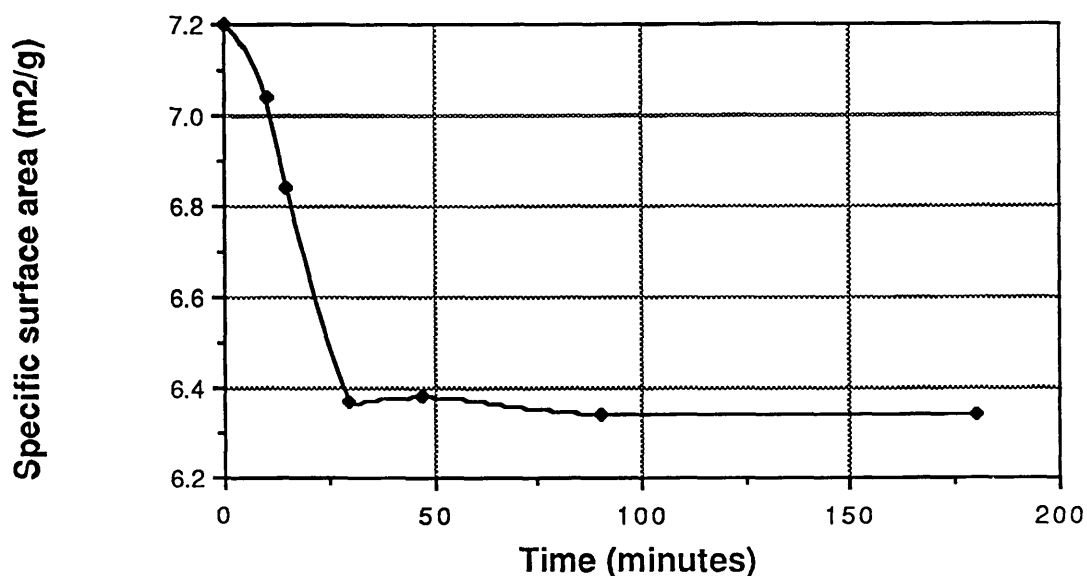


Figure 5.27 Change in specific area of Flexicoke with time; Temperature=1000°C, -150+125 μ m as-received coke size fraction, HCl partial pressure=1.0, preheating time=30 minutes.

As can be seen from Figures 5.28 and 5.29 at time zero the nickel and sulphur distributions are similar and where nickel peaks so does sulphur, confirming the results presented in Chapter 3. Figure 5.29 shows that after 90 minutes of reaction there is a considerable drop in the sulphur concentration, and it is more evenly distributed across the particle; there is however still a slightly higher sulphur concentration on the outside of the particle. Figures 5.30 and 5.31 show the vanadium distribution; unreacted coke has a very high vanadium concentration in a ring near the centre of the particle with concentrations as high as 12.2 wt% being observed in this region. After 90 minutes of reaction there is no marked concentration difference; although the concentration is slightly higher at the centre of the particle than in the outside, but the change is small in comparison with unreacted coke.

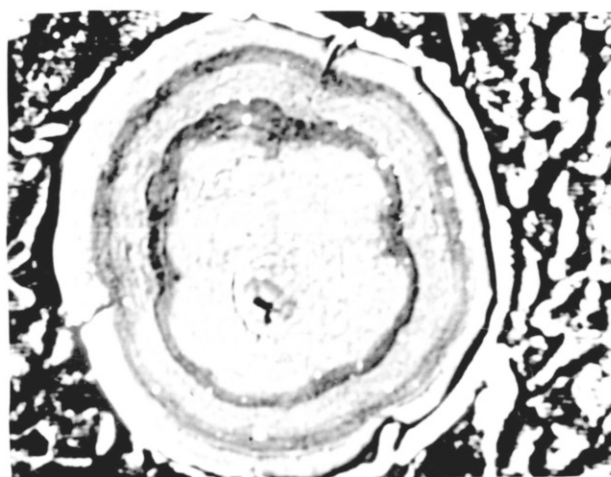


Plate 5.1 SEM of cross-section of Flexicoke particle after 90 minutes of reaction; magnification=600x.

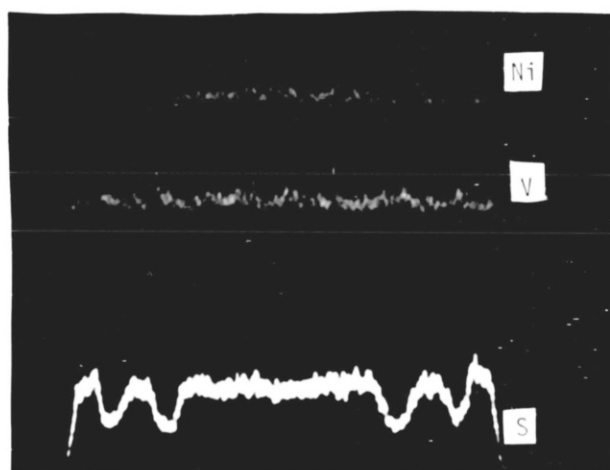


Plate 5.2 Line analysis of Ni, V and S distributions in a Flexicoke particle after 90 minutes of reaction; Magnification=600x.

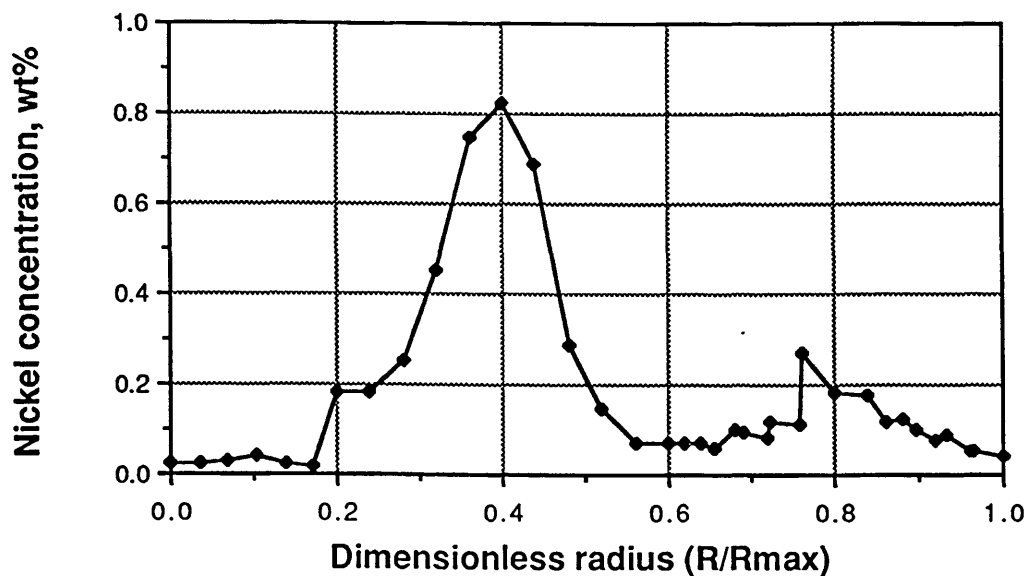


Figure 5.28 Nickel radial distribution in as-received Flexicoke; -150+125 μ m size fraction, 1000°C, HCl partial pressure=1.0, flow rate ratio=3.0.

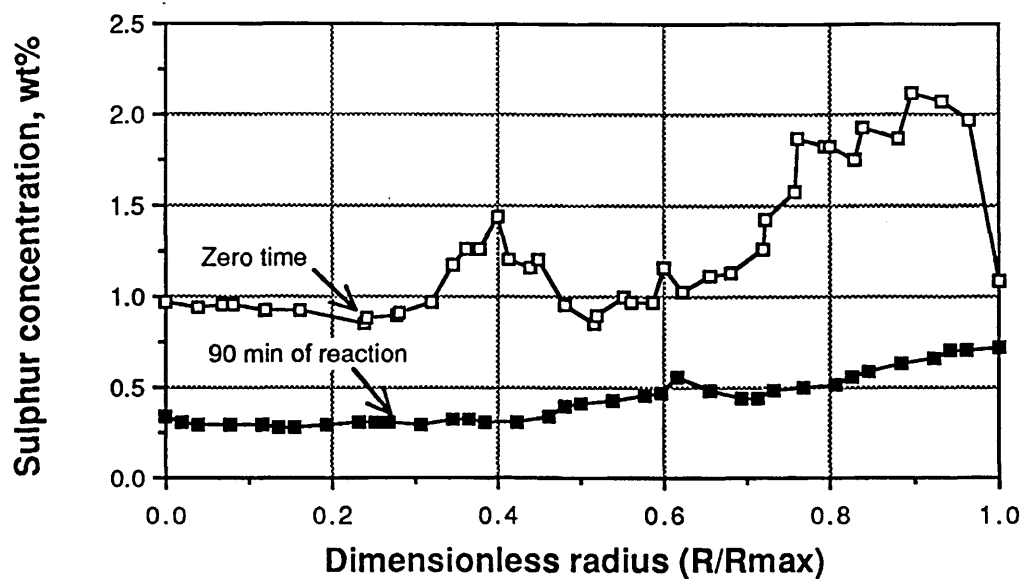


Figure 5.29 Sulphur radial distribution in as-received Flexicoke; -150+125 μ m size fraction, 1000°C, HCl partial pressure=1.0, flow rate ratio=3.0.

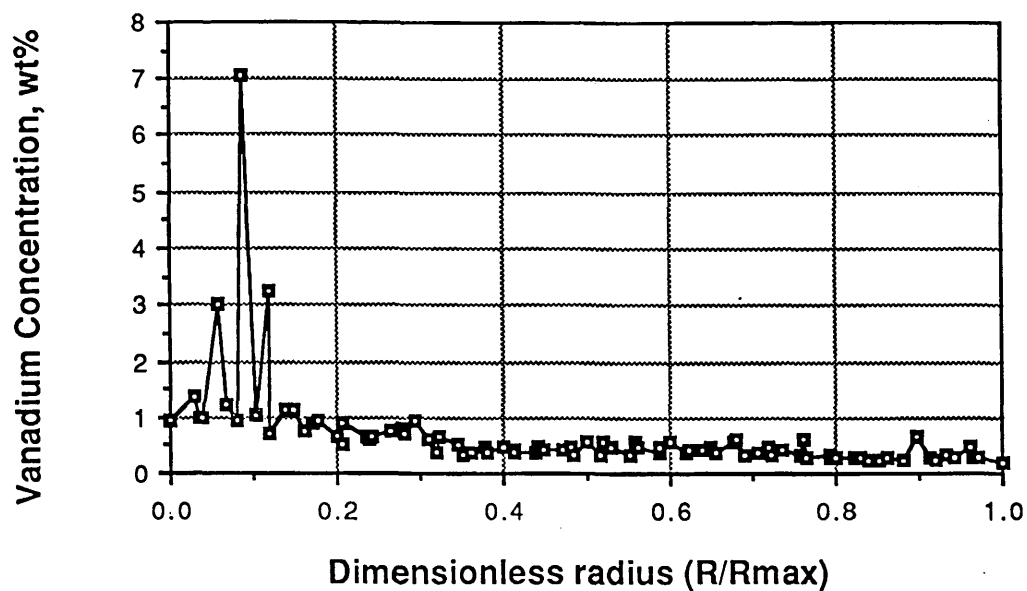


Figure 5.30 Vanadium radial distribution in as-received Flexicoke; -150+125 μ m size fraction, 1000°C, HCl partial pressure=1.0, flow rate ratio=3.0.

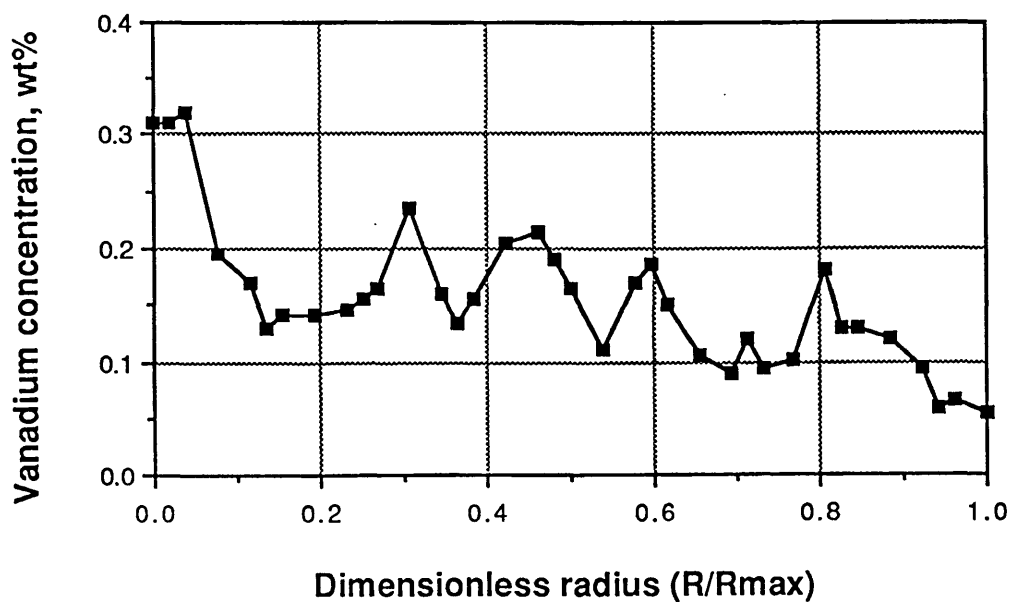


Figure 5.31 Vanadium radial distribution in as-received Flexicoke after 90 minutes of reaction; -150+125 μ m size fraction, 1000°C, HCl partial pressure=1.0, flow rate ratio=3.0.

Analysis of the exit gases from the fluidized furnace by gas chromatography, revealed the presence of a hydrocarbon with similar retention time to that for benzene or toluene; the concentration of this was low (in the order of 2-3ppm). No chloro-containing hydrocarbon compounds were detected.

The use of the fluidized bed reactor produced considerable increases in the vanadium and nickel extraction. The main reasons for this are the higher gas flow rates used, the good temperature control afforded by the fluidized reactor and the preheating of the gas. Higher extractions from ground Flexicoke are believed possible with proper control of particle size and recycle of elutriated particles.

5.5 VAPOUR TRANSPORT EXPERIMENTS USING DELAYED COKE.

A number of runs in the fixed bed apparatus were made with Delayed coke. The experimental method employed was the same as for Flexicoke. During the heating stage, a small yellow deposit formed when the furnace temperature reached about 600°C; at about 800°C large quantities of a yellow fume evolved from the coke and deposited further down the furnace. These yellow fumes were clouds of evaporated sulphur from the coke bed; the sulphur was very fine, formed a colloidal solution when mixed with acetone or sulphuric acid and was not retained by 142 filter paper (2.5µm retention). Water vapour and H₂S were also evolved during the preheating stage. No purple crystals or brown condensate were observed after the end of the reaction. A solution of the end products in 1M H₂SO₄ had a strong smell of asphalt, and when a lighted match was put to it, it caught fire giving a pale blue flame.

A fractional factorial design at two levels with six variables, the same variables and high and low levels as for factorial design 2 (Table 5.7), was started but not completed because of

the unpleasantness of the sulphur fumes. The vanadium, nickel and iron extractions obtained are given in Table 5.19 below. The extraction yields for vanadium and nickel were poor, but high iron extractions could be obtained. No further work with Delayed coke was carried out.

Treatment code	% Vanadium extraction	% Nickel extraction	% Iron extraction
abcf	12.7	21.5	53.7
ae	1.0	0.0	82.2
bcd	2.0	0.8	93.4
abce	7.1	3.1	66.8
bde	3.9	0.0	57.0
acd	0.7	0.8	12.2
abcef	9.3	7.6	84.1

Table 5.19 Vanadium, nickel and iron extraction from the vapour transport experiments using Delayed coke.

6. CONCLUSIONS.

The extraction of vanadium and nickel from Flexicoke by low temperature leaching and by a high temperature chloride vapour transport process was investigated. Additionally, some work was done on the extraction of these metals from Delayed coke.

As-received Flexicoke showed poor vanadium and nickel extractions in aqueous acid leaching. The use of oxidizing agents had little effect on the metal recovery. Higher leaching temperatures produced a small increase in the vanadium extraction, but negligible change in nickel extraction. The use of organic solvent as leaching reagents was highly ineffective; the vanadium extractions were very low, and only trace amounts of nickel were extracted. Flexicoke interacted strongly with some of the organic reagents, i.e. quinoline, forming a tar-like residue, which is accompanied by an increase in coke mass and volume of about 35% and 300%, respectively.

The extraction of vanadium and nickel from ground Flexicoke by acid leaching was more successful. Vanadium extractions as high as 78% were obtained with -53 μ m ground coke, when leached at 70°C with 1 M sulphuric acid. The leach liquors showed a deep blue colour characteristic of the oxovanadium (IV) ion, VO²⁺. Nickel extractions were still poor with the maximum extraction obtained being only 17%. The extraction of vanadium from ground Flexicoke fitted the shrinking core kinetic model quite well. Increases in acid temperature were found to increase both the vanadium extraction and extraction rate. An activation energy for the vanadium leaching reaction of 24 kJ/mol was found, indicative of a mixed kinetics situation, where the rate controlling steps are diffusion through the reacted coke layer and boundary layer diffusion and/or chemical kinetics.

The vanadium extraction and extraction rate from ground Flexicoke was found to increase with increasing sulphuric acid concentration, reach a maximum at a H_2SO_4 concentration of one mole, and then drop with further increases in the acid concentration. This unusual behaviour could be accounted for by the concentration of the neutral VOSO_4 complex in solution, which reaches a maximum at about 1 M H_2SO_4 ; further increases in H_2SO_4 concentration decreased the equilibrium concentration of VOSO_4 and increased the concentration of the anionic $\{\text{VO}(\text{SO}_4)_2\}^{2-}$ complex. This anionic complex is then absorbed by the positively charged coke surface (zero point potential for Flexicoke occurs at a pH of 0-0.5) thus producing the apparent decrease in metal extraction. The acid concentration appeared to have little effect on the nickel extraction, which were low and ranged from 3.5 to 8%.

Particle size of coke was the most influential variable in increasing the vanadium extraction; for example, an increase in acid temperature from 30° to 70°C with -53 μm ground coke produce an increase in vanadium extraction from 70 to 79%, whilst a decrease in coke size from the -106+75 μm to the -53 +45 μm size fraction produced an increase from 18% to 72%. Controlling the sulphuric acid concentration to coincide with the maximum equilibrium concentration of the VOSO_4 complex is also helpful in increasing the vanadium extraction.

The extraction of vanadium and nickel from Delayed coke by aqueous and organic leaching was highly unsuccessful; only trace amounts of vanadium were found with as-received and ground coke (-53 μm).

The extraction of vanadium and nickel from Flexicoke by a vapour transport process was found to be feasible and to give high metal recoveries under certain conditions. The main products of reaction were VCl_4 and VCl_3 . Nickel and iron are believed to be transported as NiCl_2 and FeCl_2 , sodium is also extracted from the coke. The sulphur in the coke decreases

markedly, and emissions of H_2S have been detected. The volatile products start to condense in the fluidized reactor at 550°-600°C, a temperature sufficiently lower than the reaction temperature to permit easy separation of the products from the reacted Flexicoke.

Vanadium extractions from a fixed bed of Flexicoke were found to be increased by increases in the HCl partial pressure, gas flow rate and reaction time and by decreases in coke particle size. Under fluidization conditions, HCl partial pressure, time and temperature had an effect on the vanadium extraction. The rate of reaction was also found to be affected by increases in HCl partial pressure and temperature. Decreases in particle size increased the extraction and extraction rate. The rate controlling step for vanadium extraction is affected by both temperature and HCl partial pressure. Below 900°C the extraction is chemically controlled at all HCl partial pressures. In the temperature range 900° to 1000°C the rate controlling step change from chemical control to diffusion control as the HCl partial pressure is increased. Extraction from ground coke was chemically controlled under the investigated conditions.

Nickel extractions were found to be enhanced by increases in the HCl partial pressure, gas flow rate and reaction time but decreased by the presence of water vapour. Temperature had no effect on the nickel extraction from the fixed bed but had a large effect in the fluidized bed tests. Nickel extraction was found to be chemically controlled with an activation energy of 60-70 kJ/mol. No change in the rate controlling step was observed at the temperatures and HCl partial pressures investigated. Reducing the coke particle size had no effect in the nickel extraction or extraction rate.

Both nickel and vanadium extraction rates were found to be first order with respect to HCl partial pressure. Flow rate had no effect on the vanadium extraction rate; but at low flow rates an "induction" time effect was observed for nickel extraction.

Iron extractions from a fixed bed of Flexicoke were found to be enhanced by increases in reaction time, coke particle size and the HCl partial pressure, and decreased by increases in temperature. The extraction and extraction kinetics of iron from a fluidized bed of Flexicoke were not investigated because its concentration was too low for quantitative XRF analysis.

The surface area of Flexicoke was found to increase, reach a maximum and then decrease again. The partial pressure of water vapour was highly influential in increasing the surface area of Flexicoke. No direct correlation between change in surface area and metal extraction could be found.

With the exception of vanadium, as-received Flexicoke, reacted by the vapour transport process, fulfills the typical chemical specifications for calcined petroleum cokes listed in Table 1.5. A 55-60% vanadium extraction still leaves the coke with some 4000ppm of vanadium. Canadian Fluid coke with similar vanadium concentration has been used for anode production in the Hall-Heroult process. The addition of the tar to make the anode will reduce the total vanadium concentration in the anode to about 2000-3000ppm. The sulphur concentration in the reacted Flexicoke (about 0.4 to 0.6wt%, from Figure 5.29) is particularly encouraging in promoting the use of this coke for anode production in the Hall-Heroult process.

Vanadium and nickel extractions from Delayed coke by the vapour transport method were poor; however, high iron extractions were achieved. Only limited experimentation with Delayed coke was performed because of the unpleasantness of the released volatiles during preheating.

In Flexicoke vanadium and nickel were found to be concentrated in a ring outside the seed particle, while sulphur was concentrated in the deposited coke layers. The vanadium and sulphur concentrations were found to be relatively uniform after 90 minutes of reaction in the vapour transport process.

Vanadium and nickel were found to be uniformly distributed in Delayed coke

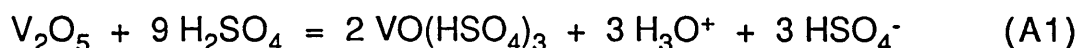
The main disadvantage of the leaching experiments is the necessity to grind the Flexicoke. The vapour transport process was quite successful, and high vanadium, nickel and iron extractions were obtained without the need to grind the coke. The use of a fluidized reactor has the extra advantage that the proposed process is compatible with existing Flexicoking technology.

APPENDIX A

SPECTROPHOTOMETRIC STUDIES OF VANADIUM (V) AND VANADIUM (IV) COMPLEXES IN SULPHURIC ACID.

A1. INTRODUCTION

It is generally recognized [116] that at low pH the predominant vanadium (V) and vanadium (IV) species are VO_2^+ ($\text{pH} \leq 1$ and $< 0.1\text{M}$ vanadium) and VO^{2+} ($\text{pH} \leq 2$), respectively, in the vanadium-water system. There is, however, little information available in the literature on the stepwise complex formation of vanadium (V) and vanadium (IV) complexes in sulphuric acid solutions. Mishra and Symons [110] have proposed from e.s.r. and optical spectral data that in 100% sulphuric acid the complexes given by reactions A1 and A2 are formed.



Conductivity data for vanadium pentoxide solutions in 100% sulphuric acid indicated a relative decrease in the number of complexing bisulphate ions with increasing concentration of V_2O_5 ; this is believed to be due to the formation of polymeric species. Gillespie et al [111] found from cryogenic and conductivity data that the average number of molecules in a complex decreased from 6.7 in dilute vanadium solutions to 5.4 at higher concentrations. Mishra and Symons showed that in dilute solutions the average number of bisulphate ion ligands was about 2.4 and their results are almost quantitatively correct for a combination of reactions A1 and A2, the former constituting about 65% of the total.

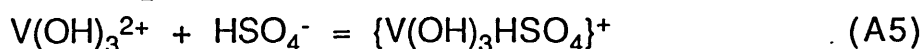
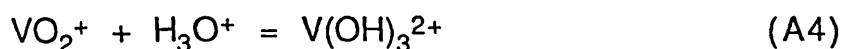
Gillespie et al [111] also proposed the formation of $\text{VO}(\text{HSO}_4)_3$ complex by reaction A1. They suggested that $\text{VO}(\text{HSO}_4)_3$ was a weak acid, and that the equilibrium given by reaction A3 would be set up. From their results for 0.01 M and 0.05 M V_2O_5 the

stability constant, K_b , for reaction A3 was found to be $(2.9 \pm 0.2) \times 10^{-2}$ mole/Kg; and the acid dissociation constant, K_a , for $\text{HVO}(\text{HSO}_4)_4$ to be 0.8×10^{-2} mole/Kg.

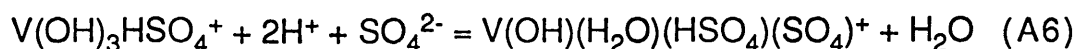


Some evidence for the formation of a dimer $\text{V}_2\text{O}_3(\text{HSO}_4)_4$ and its anion $\text{V}_2\text{O}_3(\text{HSO}_4)_5^-$, or their solvated forms, at high vanadium concentrations was presented. The presence of the $\text{V}_2\text{O}_3^{4+}$ dimer has been confirmed by Madic et al [134], who found VO_2^+ to give the dimer in H_2SO_4 and HClO_4 solutions; in the range 13 to 16 M H_2SO_4 vanadium (V) was found to totally convert to the dimeric form.

Little and Waters [113] have proposed, from observations of the kinetics of oxidation of organic compounds by vanadium (V) in aqueous sulphuric acid solutions (0 to 6 M), the presence of the $\text{V}(\text{OH})_3\text{HSO}_4^+$ complex, formed by reactions A4 and A5 below.



$\text{V}(\text{OH})_3^{2+}$ was formed by reaction of the VO_2^+ with H_3O^+ in perchloric acid. Puutio and Vitanen [114] and Mehrotra [115] also proposed reactions A4 and A5 to account for their results from similar investigations. However, Mehrotra pointed out that reaction A6 below was also consistent with the observed kinetic results.



The proposed complexes in dilute sulphuric acid solutions are based on indirect observations; no direct evidence is available to confirm the presence of these complexes.

The solid sulphate $\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$ has been extensively investigated. VOSO_4 crystallises in a solid network of VO_6 octahedra and SO_4 tetrahedra; the coordination polyhedron about the vanadium is a distorted octahedra with one short $\text{V}=\text{O}$ bond (1.59 Å) *trans* to a long $\text{V}-\text{O}$ bond (2.28 Å) and with $\text{O}-\text{V}=\text{O}$ bond angle of 99.9° . The complex $\text{VO}(\text{H}_2\text{O})_5\text{SO}_4$ occurs in three forms, one monoclinic and two orthorhombic. X-ray analysis of the monoclinic showed that the VO^{2+} group is bound to four water molecules and to the oxygen atom of a sulphate group, the latter being in one of the *cis* positions to the VO^{2+} group. The $\text{VOSO}_4 \cdot x\text{H}_2\text{O}$ solids have been recently reviewed by Vilas-Boas and Costa-Pessoa [131]. In aqueous solution the cation is the $\text{VO}(\text{H}_2\text{O})_5^{2+}$ ion; and from ^{17}O n.m.r. evidence the four equatorial water molecules have a residence time of 1.35×10^{-3} sec, whereas that of the axial water molecule is probably only about 10^{-11} sec [117].

Oxovanadium (IV) sulphate solutions were studied by Ducret [132] who concluded that the complexes VOSO_4 and $\{\text{VO}(\text{SO}_4)_2\}^{2-}$ form, and report the first stepwise stability constant, K_1 , for the $\text{VO}^{2+}-\text{SO}_4^{2-}$ system to be 63 M^{-1} . Strehlow and Wedt [133] also reported the existence of the VOSO_4 complex and found from measurements of relaxation time that an intermediate complex, $\text{VO}(\text{H}_2\text{O})\text{SO}_4$, formed; they report K_1 for the $\text{VO}^{2+}-\text{SO}_4^{2-}$ system to be $300 \pm 50 \text{ M}^{-1}$ at 25°C and zero ionic strength; and claimed that below a VOSO_4 concentration of 0.2 M little $\{\text{VO}(\text{SO}_4)_2\}^{2-}$ was present. No value for the second stepwise stability constant is reported by either author.

The ligands of interest in this study are the bisulphate and sulphate ions, and knowledge of their respective concentrations, at a given sulphuric acid concentration, is required. Values for the second dissociation constant of sulphuric acid, K_2 , have been the subject of many studies, the result of which is a large number of empirical and semi-empirical equations, which have been recently reviewed by Watts [119], over different ranges of

temperature and ionic strength, μ . For the purpose of this investigation, the equation proposed by Lindstrom and Wirth [118] (equation A7) relating K_2 to μ will be used. From this equation the bisulphate and sulphate ion concentrations can be calculated for ionic strengths up to 4 M.

$$\log K_2 = \log 0.0102 + 2.036\mu^{1/2} - 1.376\mu + 0.8862\mu^{3/2} - 0.217\mu^2 \quad (\text{A7})$$

The first dissociation of sulphuric acid is virtually complete at sulphuric acid concentrations below 11 M; there is, however, considerable uncertainty as to the value of the first dissociation constant. For high H_2SO_4 concentrations the diagram by Young [120], given in Figure A1, was used to determine the concentration of the HSO_4^- and SO_4^{2-} ions.

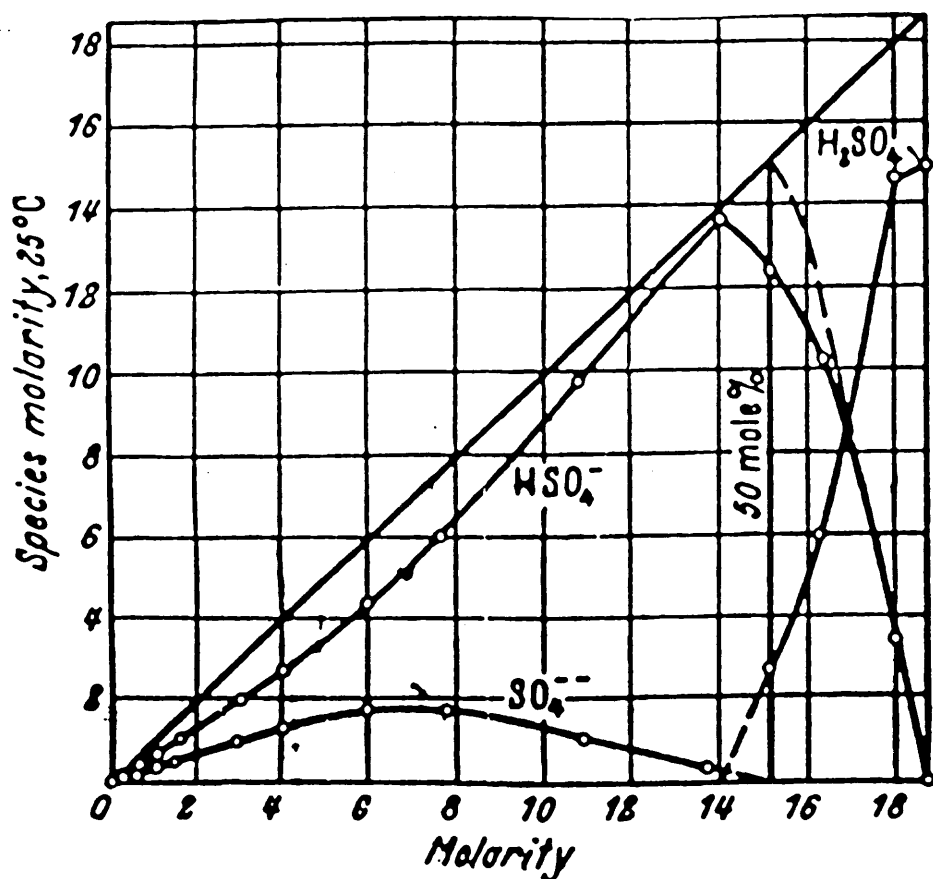


Figure A1 Proportion of H_2SO_4 molecules, HSO_4^- and SO_4^{2-} ions in aqueous sulphuric acid [120].

A2. EXPERIMENTAL

UV-Visible spectra were obtained with a Hewlett-Parkard HP-8415-A diode array spectrophotometer, which offered the advantages of very fast spectra collection (0.1 sec), storage of spectra on magnetic disk and reasonably flexible data handling facilities. The wavelength range analysed was 190 to 820nm with a wavelength resolution of 2nm. Silica cells were used for all experiments, with path lengths of 1.0 and 0.5 cm. Spectra were collected in the absorption mode. The UV lamp was allowed to warm up for 1 hour before spectra were collected; reproducibility in the absorbance readings was found to be ± 0.0005 absorbance units. Maximum absorptions were maintained below 1.5 absorbance units; where a higher absorbance was obtained the 0.5 cm cell was used. Measurements were conducted at room temperature, ($18^\circ \pm 1^\circ\text{C}$).

All solutions were prepared using grade A volumetric glassware. The metal stock solutions, containing 2.0×10^{-3} M VO_2^+ or 0.10 M VO^{2+} , were prepared by dissolving 99.9% V_2O_5 and 99.9% V_2O_4 , respectively, in a solution of 0.25 M Analar perchloric acid in double distilled water. The sulphuric acid stock solutions were prepared by weighing the required amount of concentrated Analar sulphuric acid and dissolving in double distilled water; these were approximately made up to volume, allowed to cool and then made up to one litre in a volumetric flask. 15, 10 and 5ml of the vanadium stock solutions were added to volumetric flasks, the volumes were made up to 15ml by addition of the required volume of 0.25 M Analar perchloric acid solution, and the solutions made up to 100ml by adding the required sulphuric acid stock solution. For sulphuric acid concentrations higher than 7 M, the metal and acid stock solutions were approximately made up to volume, allowed to cool and then made up to 100ml in a volumetric flask. Reference solutions were prepared by mixing 15ml of 0.25 M Analar perchloric acid solution with the sulphuric acid stock solution. The spectrophotometer automatically subtracted the reference spectra from the metal

spectra. Solutions were analysed within 24 hours of being prepared. No decomposition was observed with time, although at very high sulphuric acid concentrations the reference and stock solutions yellowed with time, presumably due to carbon oxidation by the sulphuric acid.

Molar absorption coefficients, ϵ^λ , were calculated from the absorbance readings for three different metal concentrations (at a given acid concentration), by applying Beer's law and the method of least squares. Regression coefficients greater than 99% were obtained in all cases. When calculating the HSO_4^- and SO_4^{2-} concentrations by equation A7, due account was taken of the presence of perchloric acid in calculating the ionic strength.

A3. RESULTS

A3.1 Vanadium (V) - H_2SO_4 System.

The $\text{VO}_2^+ - \text{H}_2\text{SO}_4$ solutions changed colour from pale yellow to yellow-orange as the sulphuric acid concentration was increased. Absorption curves of vanadium (V) solutions in sulphuric acid concentrations ranging from 0 to 14.7 M are given in Figure A2. At low acid concentrations, the spectra peak at a wavelength of 208nm; whilst at very high acid concentrations a slight shift in the peak wavelength to 218nm is observed. Figure A2 shows that there is very little change in the shape of the absorption curve with increasing acid concentration, although there is a larger relative increase in the shoulder at 340nm over the peak at 208nm at high sulphuric acid concentrations. Madic et al [134] have suggested that the shoulder at 340nm is associated with dimerization of VO_2^+ at high sulphuric acid concentrations.

Table A1 gives the calculated molar absorption coefficient, ϵ^λ , at various wavelengths, λ . From this data and the bisulphate ion concentrations, obtained from equation A7 and Figure A1, the

stepwise stability constants for $\text{VO}_2^+ \text{-HSO}_4^-$ complex formation may be found. In an experiment a VO_2^+ solution was mixed with a solution containing 1 M sodium sulphate in 0.25 M perchloric acid; an equilibrium would be set up between the acid and the sulphate ions to give a ligand concentration of about 0.25 M bisulphate and 0.75 M sulphate. The absorption spectra obtained from this test was a little lower to that obtained with a VO_2^+ solution in 0.43 M sulphuric acid (which contained 0.33 M HSO_4^- and 0.096 M SO_4^{2-}), Figure A3; if sulphate ions were complexing to vanadium (V) then an absorption spectra similar to that found for a VO_2^+ solution in 1.73 M sulphuric acid (which contained 1.08 M HSO_4^- and 0.65 M SO_4^{2-}) would be expected. Thus, the little change in absorption that occurred on adding the 1 M sodium sulphate solution could be accounted for by the bisulphate ion concentration which arises from the presence of the acid. This indicates that the ligand of interest is the bisulphate ion; sulphate ions either do not complex with VO_2^+ or more likely they form very weak complexes. Figure A4 shows that as the sulphuric acid concentration increases, the molar absorption coefficient also increases; at very high sulphuric acid concentrations the decrease in ϵ^λ is probably associated with a drop in the bisulphate ion concentration.

The relevant equation for the calculation of the first stepwise stability constant, K_1 , is given by equation A8; K_1 is defined by equation A9 below. Equation A8 only applies when there is only one complex present in solution, and may be used for sulphuric acid concentrations up to 5.2 M

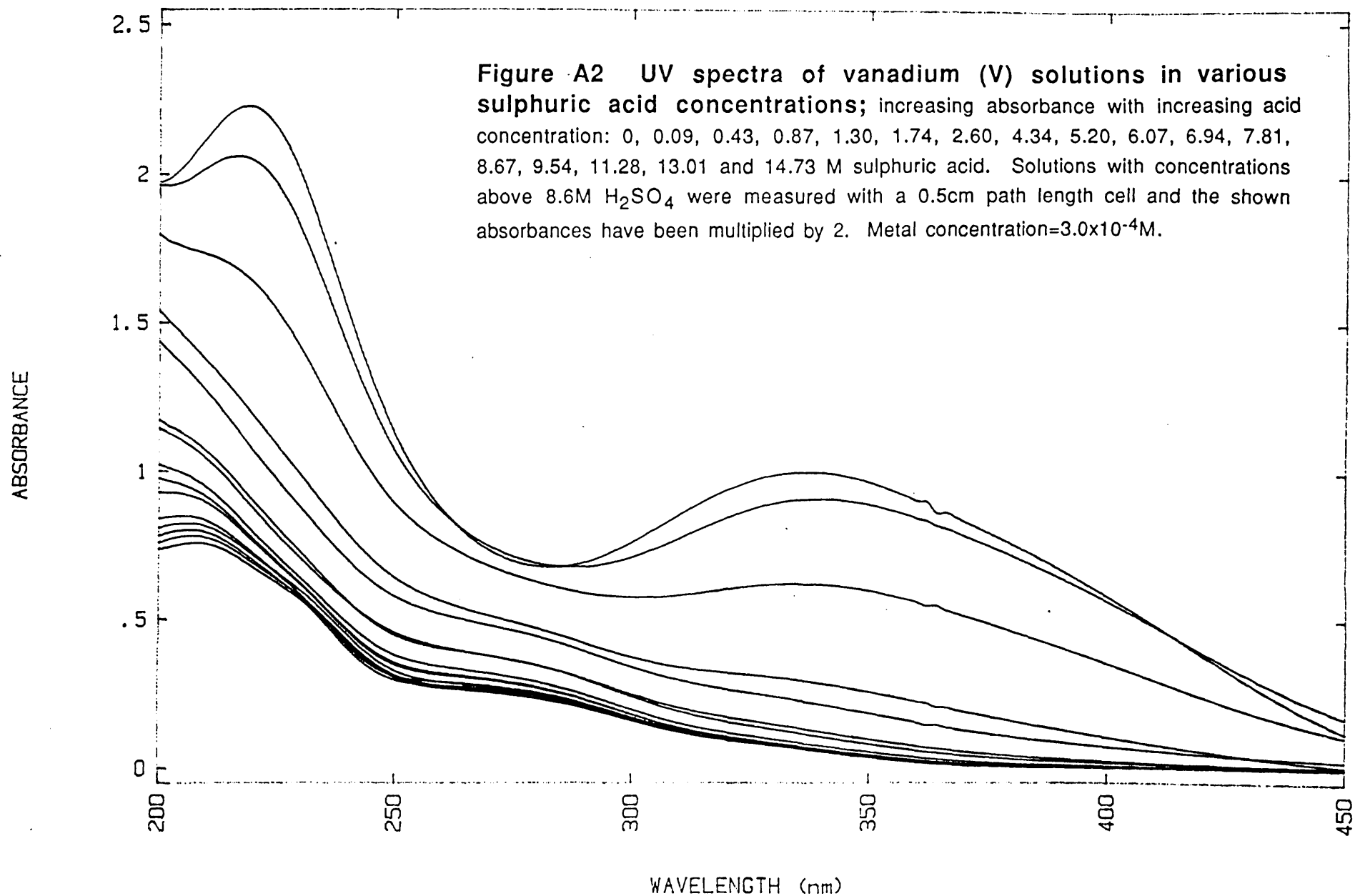
$$\frac{1}{(\epsilon^\lambda - \epsilon_0^\lambda)} = \frac{1}{(\epsilon_1^\lambda - \epsilon_0^\lambda)} + \frac{1}{K_1(\epsilon_1^\lambda - \epsilon_0^\lambda)[\text{HSO}_4^-]} \quad (\text{A8})$$

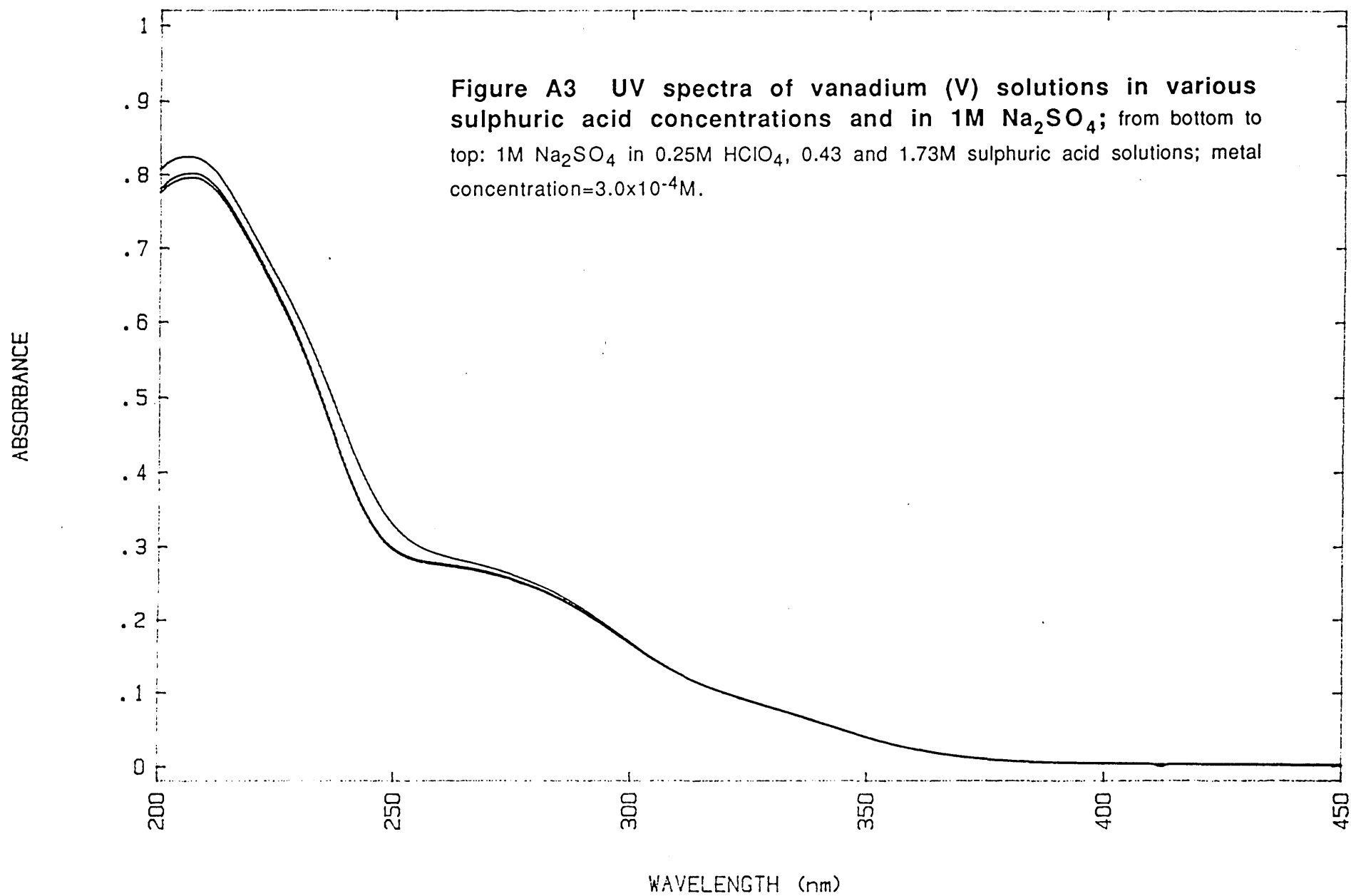
$$K_1 = \frac{[\text{VO}_2(\text{HSO}_4)]}{[\text{VO}_2^+][\text{HSO}_4^-]} \quad (\text{A9})$$

Table A1 Effect of increasing the sulphuric acid concentration on the molar absorption coefficient of vanadium (V) solutions at various wavelengths.

Sulphuric acid Concentration (M) ¹	Molar absorption coefficient, ϵ^λ (M ⁻¹ cm ⁻¹)						
	210	230	250	270	290	310	330
0	2428.7	1829.2	1003.7	818.9	651.7	388.5	240.7
0.09	2520.9	1893.9	1023.1	848.2	676.0	405.4	253.0
0.43	2646.5	1908.3	1021.0	884.1	705.8	426.6	269.4
0.87	2586.3	1912.4	1018.1	869.2	697.2	419.9	253.9
1.30	2607.0	1932.4	1043.3	885.1	708.5	426.1	267.3
1.76	2714.9	1948.3	1045.5	905.7	716.8	425.3	264.1
2.60	2778.6	1966.1	1062.0	920.6	727.0	428.7	265.7
4.34	2985.5	1984.0	1087.1	981.2	770.0	450.2	276.4
5.20	3051.5	2129.0	1210.9	1036.5	775.9	455.7	280.3
6.07	3158.2	2217.0	1297.3	1102.0	829.7	657.7	322.5
6.94	3567.0	2378.2	1428.0	1212.7	996.9	636.9	435.4
7.81	3480.9	2546.9	1618.7	1367.8	1003.4	677.7	489.9
8.67	4231.4	2871.7	1873.4	1547.1	1313.3	985.2	803.1
9.54	4572.4	3240.6	2098.5	1673.5	1399.7	1127.0	1012.9
11.28	5528.6	4469.6	2838.3	2191.9	1965.7	1940.6	2067.2
13.01	6404.9	5684.1	3399.8	2369.4	2263.3	2579.9	2977.9
14.74	5883.3	5450.8	3029.1	1931.7	2309.8	2843.6	3293.1

¹ The solution for 0 M sulphuric acid was prepared in 0.25 M perchloric acid; all other solutions contained 0.0375 M perchloric acid.





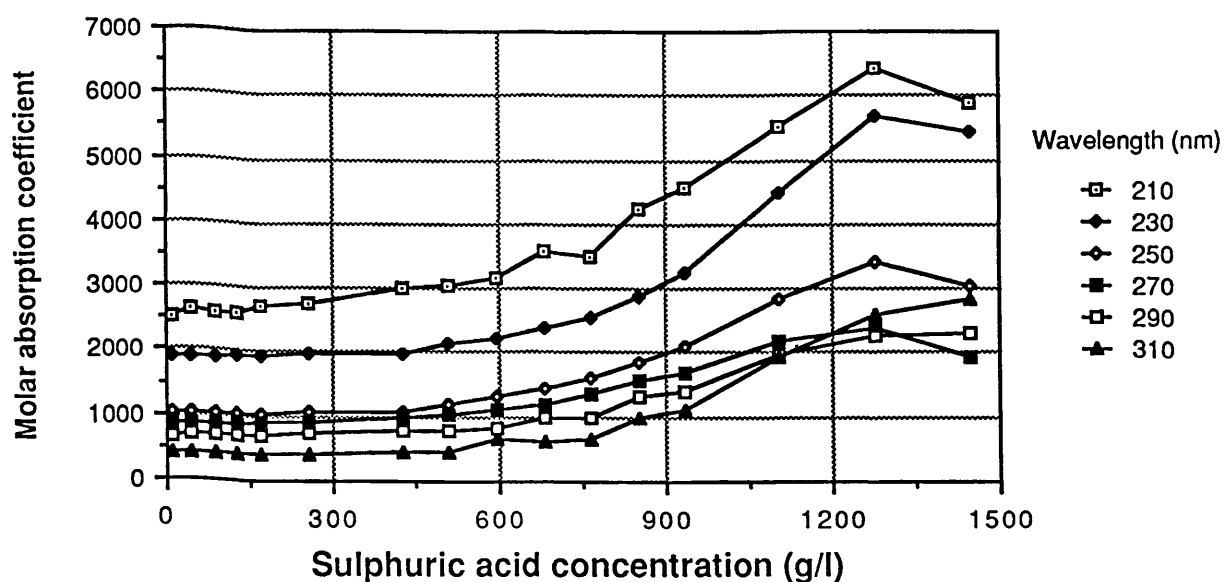


Figure A4 Effect of the sulphuric acid concentration on the molar absorption coefficient for the $\text{VO}_2^+-\text{H}_2\text{SO}_4$ system.

Figure A5 shows a plot of $1/(\epsilon^\lambda - \epsilon_0^\lambda)$ versus $1/[\text{HSO}_4^-]$; from the slope and intercept of the straight lines obtained K_1 can be calculated. The slopes and intercepts were found by the method of least squares, and their values, together with the regression coefficients, calculated K_1 and molar absorption coefficients for the VO_2HSO_4 complex, ϵ_1^λ , as a function of wavelength are given in Table A2.

As can be seen in Table A2 the stepwise stability constant, K_1 , shows a great deal of scatter; reasons for this will be discussed in Section A4. The average value for K_1 was found to be $0.824 \pm 0.553 \text{ M}^{-1}$. This value will be used for all subsequent calculations.

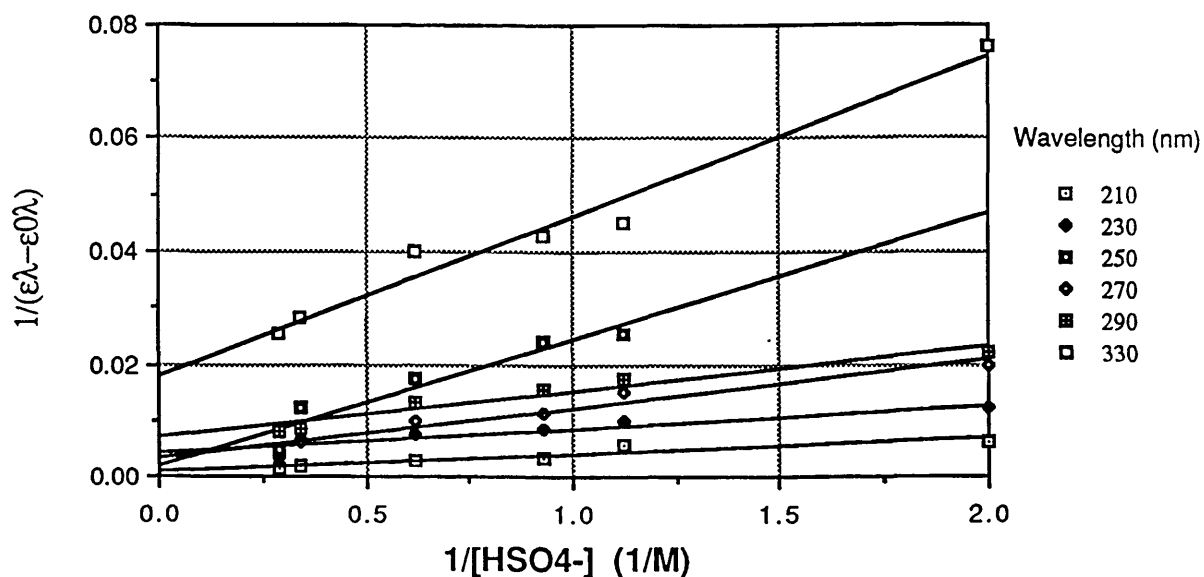


Figure A5 Plot of $1/(\epsilon^\lambda - \epsilon_0^\lambda)$ versus $1/[\text{HSO}_4^-]$ to determine K_1 for the $\text{VO}_2^+ - \text{H}_2\text{SO}_4$ system.

Wavelength (nm)	Slope $\times 10^3$	Intercept $\times 10^3$	% Regression coefficient	K_1 (M^{-1})	ϵ_1^λ ($\text{M}^{-1}\text{cm}^{-1}$)
210	2.91	1.04	94.3	0.36	3386.5
230	3.41	5.35	99.1	1.57	2016.1
250	18.40	4.33	99.0	0.24	1234.5
270	8.69	3.49	97.6	0.40	1105.5
290	8.20	6.89	96.6	0.84	796.8
310	14.97	12.08	89.3	0.81	471.3
330	17.54	27.31	95.1	1.56	277.3

Table A2 Calculated K_1 , ϵ_1^λ , and slopes and intercepts from Figure A5, for the $\text{VO}_2^+ - \text{H}_2\text{SO}_4$ system.

The second stability constant, K_2 , can be calculated by means of equation A10 below; K_2 is defined by equation A11. Equation A10 was found to be valid for the sulphuric acid concentration range 5.2 to 13.0 M.

$$K_1 K_2 \epsilon^\lambda - K_1 K_2 \epsilon_2^\lambda = \frac{(\epsilon^\lambda - \epsilon_0^\lambda)}{[\text{HSO}_4^-]^2} + \frac{K_1(\epsilon^\lambda - \epsilon_1^\lambda)}{[\text{HSO}_4^-]} \quad (\text{A10})$$

$$K_2 = \frac{[\text{VO}_2(\text{HSO}_4)_2^-]}{[\text{VO}_2(\text{HSO}_4)][\text{HSO}_4^-]} \quad (\text{A11})$$

Figure A6 gives a plot of the molar absorption coefficient, ϵ^λ , versus the right hand side of equation A10; from the slope of the lines in Figure A6 the K_2 value can be calculated. The slopes, intercepts, regression coefficients and calculated values of K_2 and ϵ_2^λ are given as a function of wavelength in Table A3.

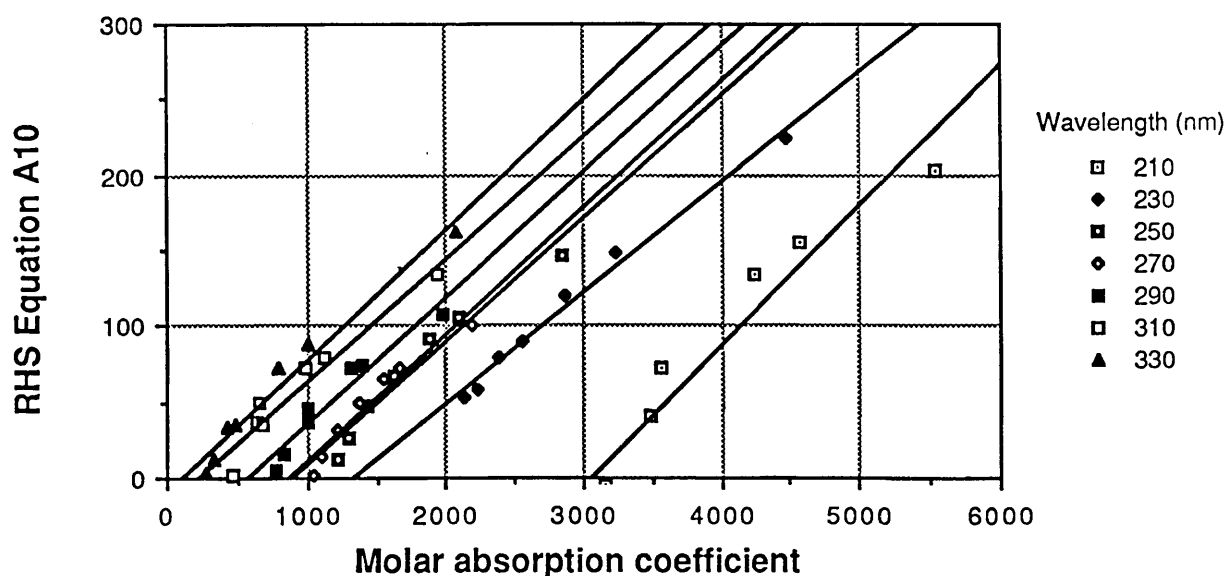


Figure A6 Plot of ϵ^λ versus the RHS of equation A10 for determining K_2 for the $\text{VO}_2^+-\text{H}_2\text{SO}_4$ system.

Wavelength (nm)	Intercept	Slope	% Regression coefficient	K ₂ (M ⁻¹)	ε ₂ ^λ (M ⁻¹ cm ⁻¹)
210	-283.9	0.093	96.4	0.113	3411.3
230	-97.8	0.073	99.4	0.089	1174.5
250	-72.4	0.081	97.6	0.099	869.6
270	-73.1	0.084	96.9	0.102	878.4
290	-47.8	0.083	96.7	0.101	573.9
310	-16.8	0.081	96.9	0.098	202.2
330	-8.4	0.086	98.7	0.104	100.9

Table A3 Calculated K₂, ε₂^λ, and slopes and intercepts from Figure A6, for the VO₂⁺-H₂SO₄ system.

The average value for K₂ was found to be 0.101 ± 0.007 M⁻¹. The standard deviation was surprisingly low considering the large error found in calculating K₁.

Equation A12 was used to calculate the third stepwise stability constant, K₃, which is defined in equation A13 below.

$$\frac{(\epsilon^\lambda - \epsilon_0^\lambda)}{[\text{HSO}_4^-]^3} + \frac{K_1(\epsilon^\lambda - \epsilon_1^\lambda)}{[\text{HSO}_4^-]^2} + \frac{K_1 K_2(\epsilon^\lambda - \epsilon_2^\lambda)}{[\text{HSO}_4^-]} = K_1 K_2 K_3(\epsilon_3^\lambda - \epsilon^\lambda) \quad (\text{A12})$$

$$K_3 = \frac{[\text{VO}_2(\text{HSO}_4)_3^{2-}]}{[\text{VO}_2(\text{HSO}_4)_2^-][\text{HSO}_4^-]} \quad (\text{A13})$$

Equation A12 requires a plot of the molar absorption coefficient, ε^λ, versus the left hand side of the equation to give a straight line with a negative slope and a positive intercept.

No such fit was obtained and thus no further analysis of the data was conducted.

From the overall stability constants, distribution diagrams may be drawn by using equations A14 to A20 below; in these equations α_n is the fraction of complex n present in solution, and C is the total vanadium concentration. Figures A7 and A8 show the stability field and complex distribution diagrams, respectively, for the $\text{VO}_2^+-\text{H}_2\text{SO}_4$ system. $\text{p}[\text{H}_2\text{SO}_4]$ is defined as the $-\log$ [sulphuric acid concentration (moles)].

$$[\text{VO}_2(\text{HSO}_4)] = \beta_1[\text{VO}_2^+][\text{HSO}_4^-] \quad (\text{A14})$$

$$[\text{VO}_2(\text{HSO}_4)_2^-] = \beta_2[\text{VO}_2^+][\text{HSO}_4^-]^2 \quad (\text{A15})$$

$$C = [\text{VO}_2^+] + [\text{VO}_2(\text{HSO}_4)] + [\text{VO}_2(\text{HSO}_4)_2^-] \quad (\text{A16})$$

$$C = [\text{VO}_2^+] (1 + \beta_1[\text{HSO}_4^-] + \beta_2[\text{HSO}_4^-]^2) \quad (\text{A17})$$

$$\alpha_0 = \frac{[\text{VO}_2^+]}{C} = \frac{1}{1 + \beta_1[\text{HSO}_4^-] + \beta_2[\text{HSO}_4^-]^2} \quad (\text{B18})$$

$$\alpha_1 = \frac{[\text{VO}_2(\text{HSO}_4)]}{C} = \beta_1[\text{HSO}_4^-]\alpha_0 \quad (\text{A19})$$

$$\alpha_2 = \frac{[\text{VO}_2(\text{HSO}_4)_2^-]}{C} = \beta_2[\text{HSO}_4^-]^2\alpha_0 \quad (\text{A20})$$

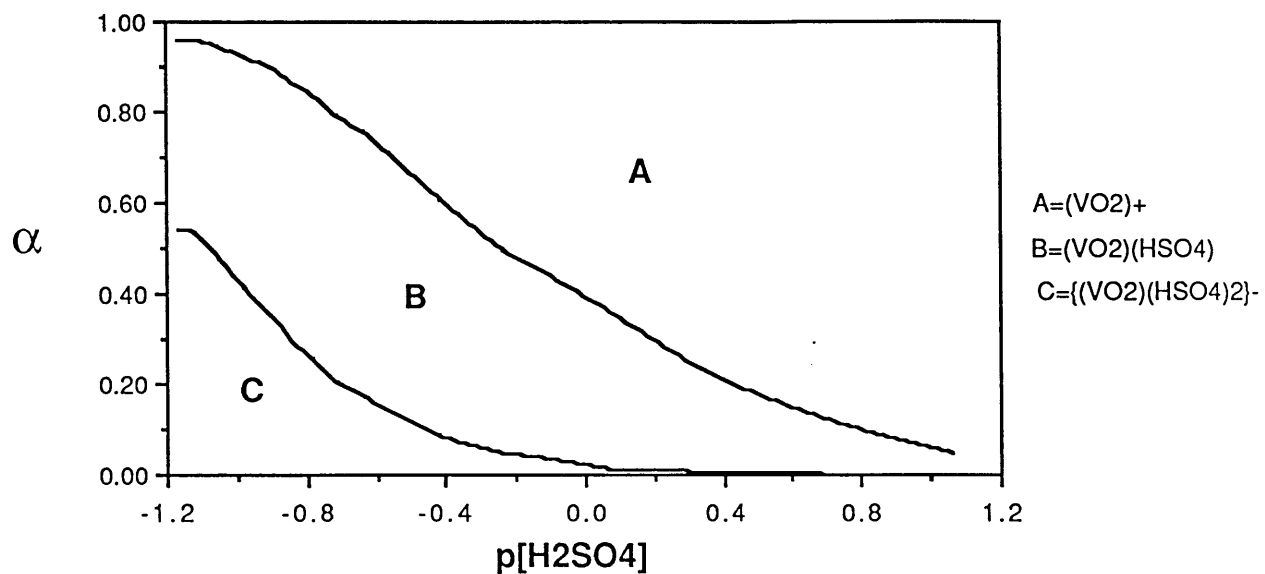


Figure A7 Stability field diagram for the vanadium (V) complexes formed in aqueous sulphuric acid solutions.

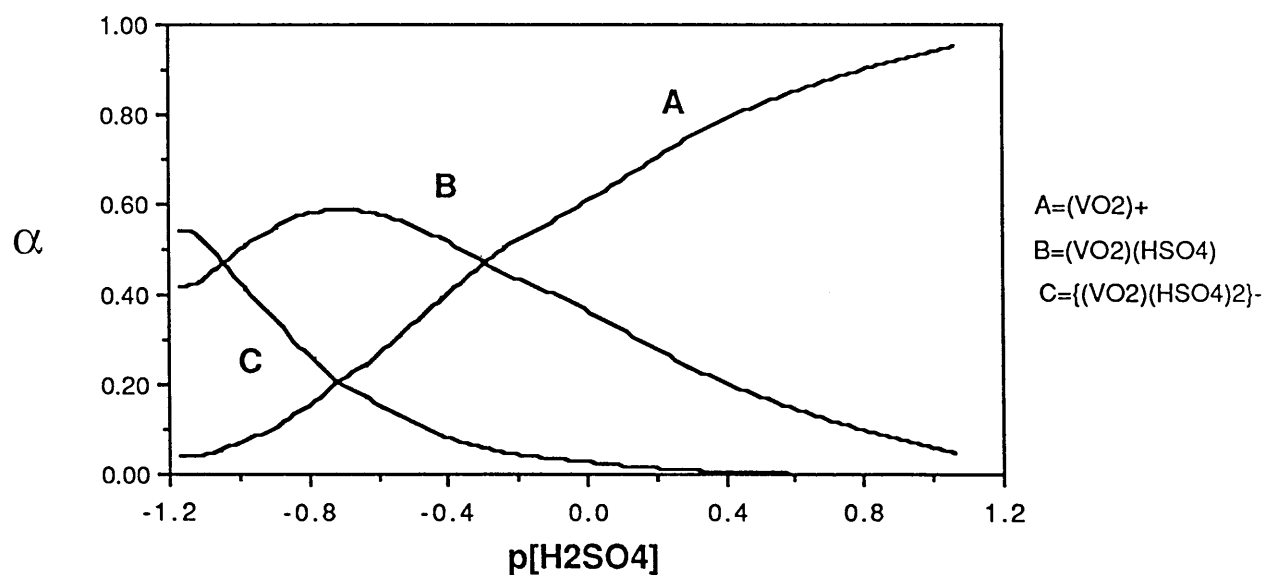


Figure A8 Distribution diagram for the vanadium (V) complexes formed in aqueous sulphuric acid solutions.

In order to determine the error of the overall stability constants, β_n , an analysis of variance has to be performed. Consider a linear function of random variables:

$$Y = \theta_0 + \theta_1 y_1 + \theta_2 y_2 + \theta_3 y_3 \quad (\text{A21})$$

where $\theta_0, \theta_1, \theta_2$, and θ_3 are constants and y_1, y_2 and y_3 are random variables. The variance of Y is given by equation A22 below:

$$V(Y) = \theta_1^2 V(y_1) + \theta_2^2 V(y_2) + \theta_3^2 V(y_3) + 2\theta_1 \theta_2 \text{Cov}(y_1 y_2) + 2\theta_1 \theta_3 \text{Cov}(y_1 y_3) + 2\theta_2 \theta_3 \text{Cov}(y_2 y_3) \quad (\text{A22})$$

where $V(y_u)$ and $\text{Cov}(y_u y_v)$ stand for the variance of y_u and covariance of y_u and y_v , respectively. If y_1, y_2 and y_3 are assumed to be uncorrelated, then equation A22 becomes:

$$V(Y) = \theta_1^2 V(y_1) + \theta_2^2 V(y_2) + \theta_3^2 V(y_3) \quad (\text{A23})$$

Thus, the variance for a linear function of random variables may be calculated. No such expression exists for a nonlinear function, such as that for the calculation of $\beta_n (=K_1 K_2 \dots K_n)$. Furthermore, in calculating β_n the values of $\beta_1, \beta_2, \dots, \beta_{n-1}$ and $\epsilon_1, \epsilon_2, \dots, \epsilon_{n-1}$ are required, and so $\beta_1, \beta_2, \dots, \beta_n$ are not independent variables. Box, Hunter and Hunter [122] have dealt with propagation of error in nonlinear functions by assuming that over a narrow range the functions are linear, and performing a test for linearity. Assume the β_n function is linear over a range of $\pm 3\sigma_y$, which is arbitrarily chosen so as to include most of the error distribution. β_2 can be represented graphically by a curved surface; over a small region it is approximated to a plane, with equation:

$$Y = Y_0 + \theta_1 (y_1 - y_{10}) + \theta_2 (y_2 - y_{20}) \quad (\text{A24})$$

where y_{10} and y_{20} are the mean values of K_1 and K_2 , respectively;

and θ_1 and θ_2 are the gradients of the plane. θ_1 and θ_2 may be determined using calculus, but for this purpose they are better obtained numerically:

$$\theta_1 = \frac{Y_1 - Y_3}{2 d_1} \quad \theta_2 = \frac{Y_2 - Y_4}{2 d_2} \quad (\text{A25})$$

where Y_1 and Y_3 are the Y values at $y_{10}+3\sigma_1$ and $y_{10}-3\sigma_1$, respectively; Y_2 and Y_4 are the Y values at $y_{20}+3\sigma_2$ and $y_{20}-3\sigma_2$, respectively; and d_1 and d_2 are $3\sigma_1$ and $3\sigma_2$, respectively. The calculation of the error is best represented in the form of a table, as shown in Table A4 below. The calculations shown in Table A4 assume that $s_y = \sigma_y$. Thus, from equation A23, the variance of $\beta_2 = V(Y)$ becomes:

$$V(Y) = (0.553)^2(0.101)^2 + (0.824)^2(0.0072)^2 = 3.154 \times 10^{-3}$$

and hence $\sigma(\beta_2) = V(Y)^{1/2} = 0.0562$. The close agreement between the differences (between $y_{10}+3\sigma_1$ and y_{10} , y_{10} and $y_{10}-3\sigma_1$; and $y_{20}+3\sigma_2$ and y_{20} , y_{20} and $y_{20}-3\sigma_2$) in Table A4 indicate that a plane provides a good approximation for the β_2 function.

		Value of Y	Difference	Gradient
$y_{10}+3\sigma_1$	2.483	0.2508	0.1676	$\theta_1=0.101$
y_{10}	0.824	0.0832		
$y_{10}-3\sigma_1$	-0.835	-0.0843	0.1675	
$y_{20}+3\sigma_2$	0.1226	0.101	0.0178	$\theta_2=0.824$
y_{20}	0.101	0.0832		
$y_{20}-3\sigma_2$	0.0794	0.0654	0.0178	

Table A4 Error analysis in the calculation of β_2 in the $\text{VO}_2^+-\text{HSO}_4^-$ system.

The above results can be summarized by listing the stepwise and overall stability constants, K_n and β_n , respectively:

$$\begin{array}{ll} K_1 = 0.824 \pm 0.553 \text{ M}^{-1} & \beta_1 = K_1 = 0.824 \pm 0.553 \text{ M}^{-1} \\ K_2 = 0.101 \pm 0.0072 \text{ M}^{-1} & \beta_2 = K_1 K_2 = 0.0832 \pm 0.0562 \text{ M}^{-2} \end{array}$$

A3.2 Vanadium (IV)- H_2SO_4 System.

The colour of the VO^{2+} - H_2SO_4 solutions changed from a pale blue to bright green as the sulphuric acid concentration was increased. The absorption spectra for vanadium (IV) solutions in sulphuric acid concentrations ranging from 0 to 14.7 M are given in Figure A9. There is little change in the shape of the absorption spectra up to H_2SO_4 concentrations of 9.5 M, but at 14.7 M sulphuric acid there is a considerable change in the shape of the absorption curve. Furthermore, at H_2SO_4 concentrations greater than 8 M there is a marked increase in the absorbance in the 450 to 500nm wavelength range. The complex formation was followed at five different wavelengths: 630, 700, 730, 750 and 770nm. Between $\lambda=630$ and 700nm no measurements were made because of disturbances in the spectra introduced by a fault in the electronics of the spectrophotometer.

The molar absorption coefficients for the VO^{2+} - H_2SO_4 system, ϵ^λ , are given as a function of acid concentration and wavelength in Table A5. An experiment in which a VO^{2+} solution was mixed with 1 M sodium sulphate solution in 0.25 M perchloric acid, showed an absorption spectra similar to that obtained with a VO^{2+} solution in 1.73 M sulphuric acid (which contained 1.08 M HSO_4^- and 0.65 M SO_4^{2-}), Figure A10, thus showing that the sulphate ligand complexes with VO^{2+} . Figure A11 gives a plot of the sulphuric acid concentration versus ϵ^λ , and it shows that at high H_2SO_4 concentrations ϵ^λ increases as the acid concentration increases, even though the sulphate concentration is decreasing,

thus indicating that that in the $\text{VO}^{2+}\text{-H}_2\text{SO}_4$ system both the sulphate and bisulphate ions are the ligands of interest.

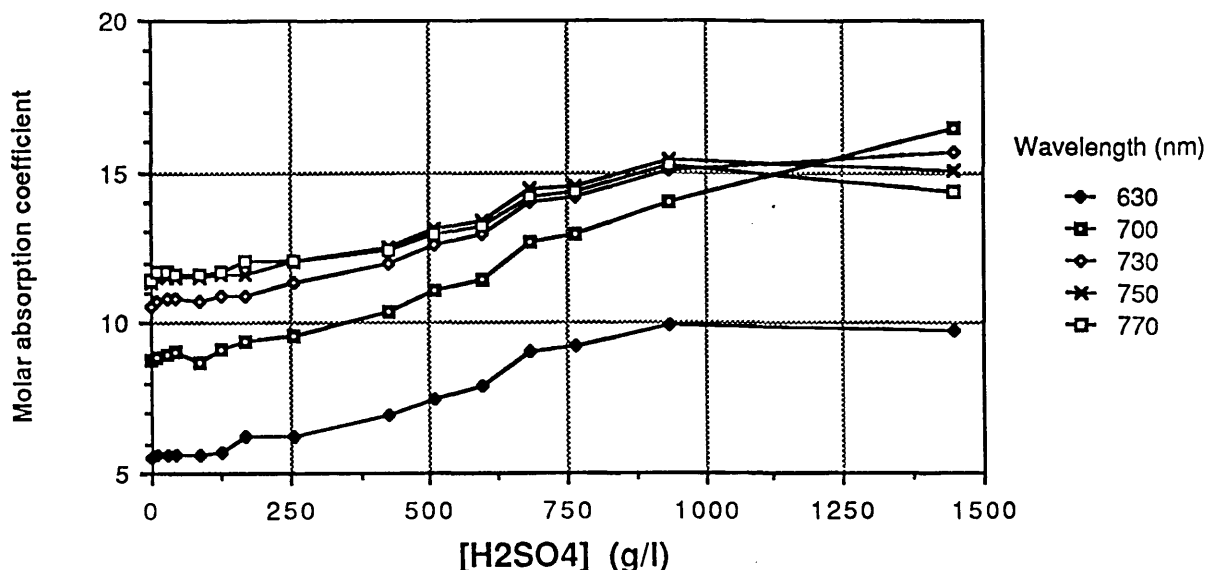


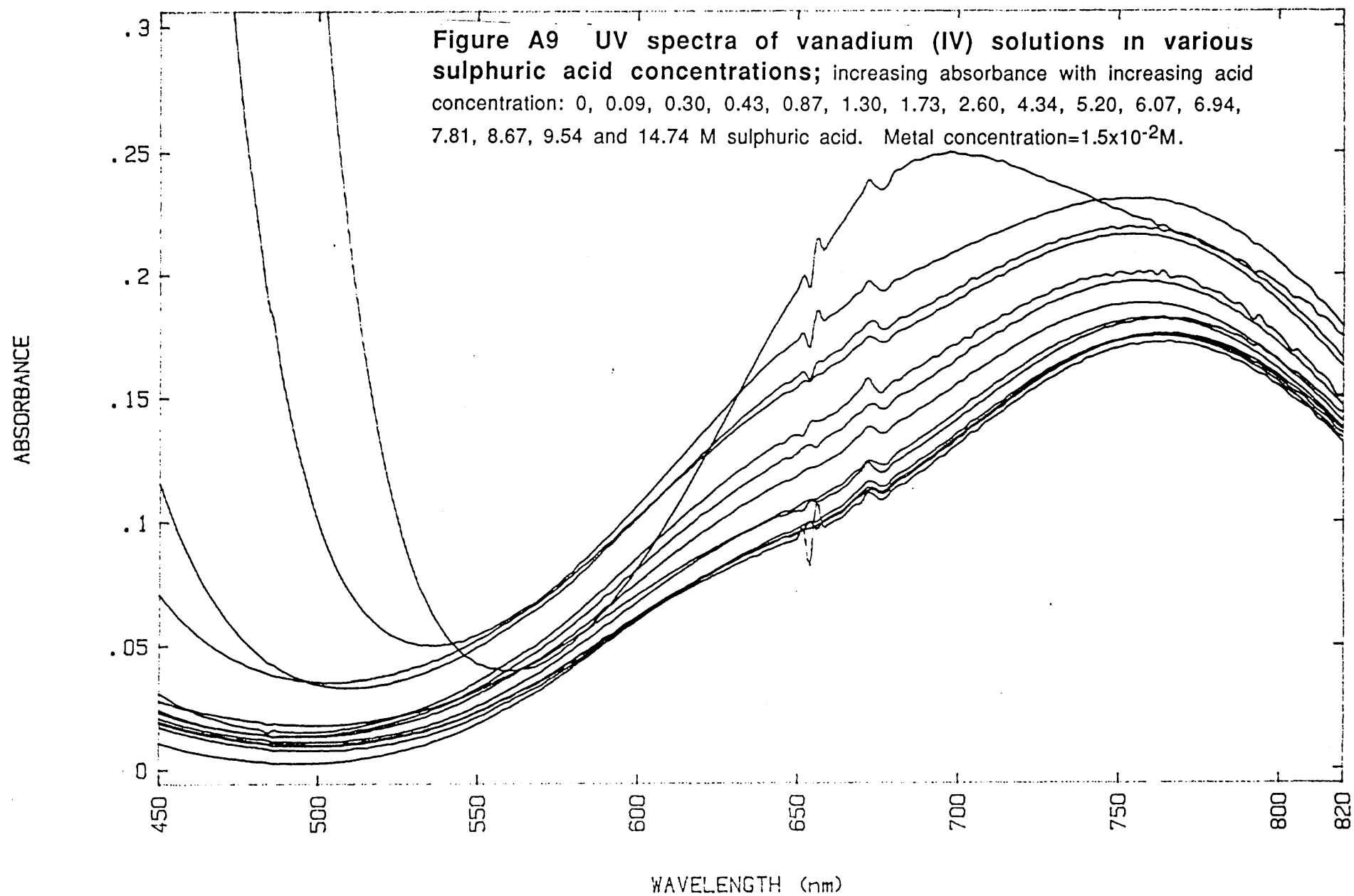
Figure A11 Plot of the molar absorption coefficient versus the sulphuric acid concentration, for the $\text{VO}^{2+}\text{-H}_2\text{SO}_4$ system.

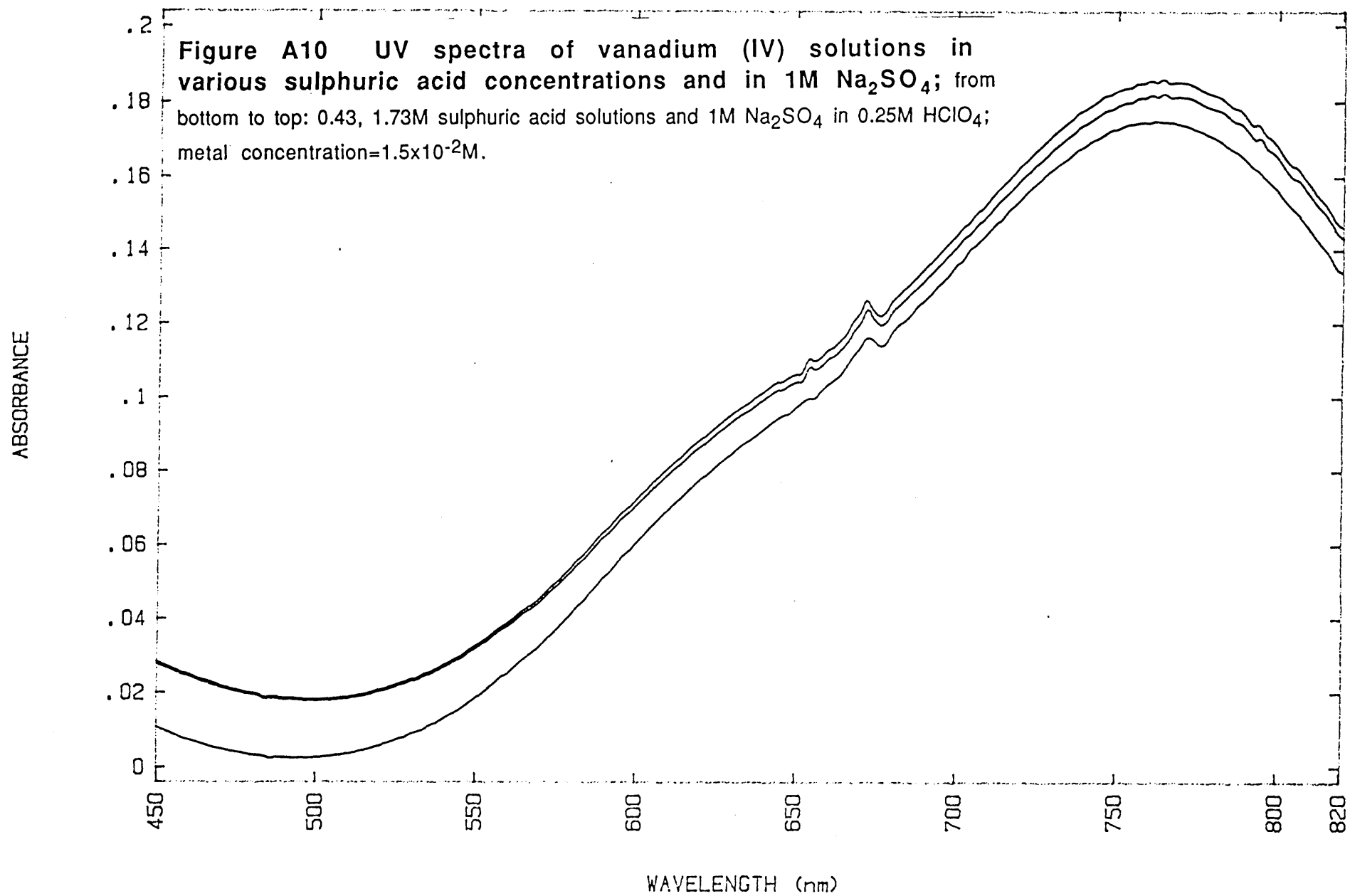
Equation A8, which was used to calculate the first stepwise stability constant for the $\text{VO}_2^+\text{-HSO}_4^-$ system, can not be applied to the $\text{VO}^{2+}\text{-H}_2\text{SO}_4$ system because there will be more than one complex species present in solution in the same acid concentration range. To study the mixed $\text{VO}^{2+}\text{-HSO}_4^-$ and $\text{VO}^{2+}\text{-SO}_4^{2-}$ system a number of different techniques would be required, such as Raman spectrophotometry, ^{51}V nuclear magnetic resonance, etc. Since this data is not available, it will be assumed that the sulphate complexes are much more stable than the bisulphate complexes. This assumption is reasonable because under most conditions the sulphate ion acts as a bidentate ligand, producing, through the chelate effect, much more stable metal complexes. Thus, with this assumption in mind the data can be processed in a similar manner as for the $\text{VO}_2^+\text{-HSO}_4^-$ system.

Table A5 Effect of increasing the sulphuric acid concentration on the molar absorption coefficient of vanadium (IV) solutions at various wavelengths.

Sulphuric acid Concentration (M) ¹	Molar absorption coefficient, ϵ^λ (M ⁻¹ cm ⁻¹)				
	630	700	730	750	770
0	5.495	8.756	10.576	11.336	11.456
0.09	5.607	8.906	10.726	11.516	11.674
0.30	5.647	9.059	10.817	11.527	11.599
0.43	5.603	8.729	10.770	11.528	11.645
0.87	5.642	8.941	10.785	11.558	11.711
1.30	5.747	9.132	10.904	11.635	11.734
1.73	6.236	9.421	10.904	11.640	12.098
2.60	6.205	9.628	11.361	12.031	12.047
4.34	6.929	10.386	11.935	12.498	12.402
5.20	7.465	11.047	12.578	13.101	12.956
6.07	7.929	11.423	12.901	13.378	13.234
6.94	9.083	12.653	13.975	14.409	14.197
7.81	9.235	12.949	14.173	14.562	14.374
9.54	9.957	13.973	15.045	15.388	15.202
14.74	9.726	16.481	15.712	15.030	14.349

¹ The solution for 0 M sulphuric acid was prepared in 0.25 M perchloric acid; all solutions contained 0.0375 M perchloric acid.





A3.2 a) The $\text{VO}^{2+}\text{-SO}_4^{2-}$ system.

From a plot of $1/(\epsilon^\lambda - \epsilon_0^\lambda)$ versus $1/[\text{SO}_4^{2-}]$ the first stepwise stability constant, K_1 , for the $\text{VO}^{2+}\text{-SO}_4^{2-}$ system can be calculated using equation A8 (substituting the $[\text{SO}_4^{2-}]$ for the $[\text{HSO}_4^-]$). Equation A8 was found to be valid for sulphuric acid concentrations up to about 1.3 M. The slopes and intercepts were found by the method of least squares, and their values, together with the regression coefficients, calculated K_1 and molar absorption coefficients for the VOSO_4 complex, ϵ_1^λ , as a function of wavelength, are given in Table A6 below.

The average K_1 value for the $\text{VO}^{2+}\text{-SO}_4^{2-}$ system was found to be $67.69 \pm 46.05 \text{ M}^{-1}$. Again the standard deviation was very high; this value will, however, be used in subsequent calculations.

Wavelength (nm)	Intercept	Slope $\times 10^2$	% Regression coefficient	K_1 (M^{-1})	ϵ_1^λ ($\text{M}^{-1}\text{cm}^{-1}$)
630	5.76	7.60	99.9	75.75	5.67
700	2.33	10.42	99.9	22.34	9.19
730	3.15	8.80	98.2	35.76	10.89
750	3.42	5.35	97.0	63.92	11.63
770	3.55	2.52	99.9	140.68	11.74

Table A6 Calculated K_1 , ϵ_1^λ , and slopes and intercepts from a $1/(\epsilon^\lambda - \epsilon_0^\lambda)$ versus $1/[\text{SO}_4^{2-}]$ plot, for the $\text{VO}^{2+}\text{-SO}_4^{2-}$ system.

The second stepwise stability constant, K_2 , was found by using equation A10. This equation was found to be valid in the sulphuric acid concentration range of 1.3 to 6.1 M. The average

K_2 value obtained from such calculations was $0.550 \pm 0.057 \text{ M}^{-1}$; the slopes and intercept of the plot required to calculate K_2 , and the K_2 and ϵ_2^λ values at various wavelengths are given in Table A7.

As for the $\text{VO}_2^+-\text{HSO}_4^-$ system no reasonable correlation was obtained in the calculation of K_3 values, thus no further analysis of the data was conducted.

Wavelength (nm)	Intercept	Slope	% Regression coefficient	K_2	ϵ_2^λ
630	-260.90	42.48	99.5	0.628	7.01
700	-384.50	39.65	94.6	0.586	10.33
730	-391.10	34.82	97.5	0.514	10.51
750	-433.70	36.25	96.1	0.536	11.65
770	-391.40	32.86	89.9	0.485	10.52

Table A7 Calculated K_2 , ϵ_2^λ , and slopes and intercepts, for the $\text{VO}^{2+}-\text{SO}_4^{2-}$ -system.

The above results can be summarized by listing the stepwise and overall stability constants, K_n and β_n , respectively. The standard deviation for β_2 was found in a similar manner as for the $\text{VO}_2^+-\text{HSO}_4^-$ system; good linearity was obtained.

$$\begin{array}{ll} K_1 = 67.69 \pm 46.05 \text{ M}^{-1} & \beta_1 = K_1 = 67.69 \pm 46.05 \text{ M}^{-1} \\ K_2 = 0.550 \pm 0.057 \text{ M}^{-1} & \beta_2 = K_1 K_2 = 37.22 \pm 25.32 \text{ M}^{-2} \end{array}$$

The value for K_1 is in good agreement with that found by Ducret [132], who obtained a value of 63 M^{-1} by dissolving VOSO_4 in weak sulphuric acid solutions; justifying, thus, the assumption made that the predominant complexes in solution are the sulphate complexes.

Figures A12 and A13 show the stability field and complex distribution diagrams, respectively, for the $\text{VO}^{2+}\text{-SO}_4^{2-}$ system.

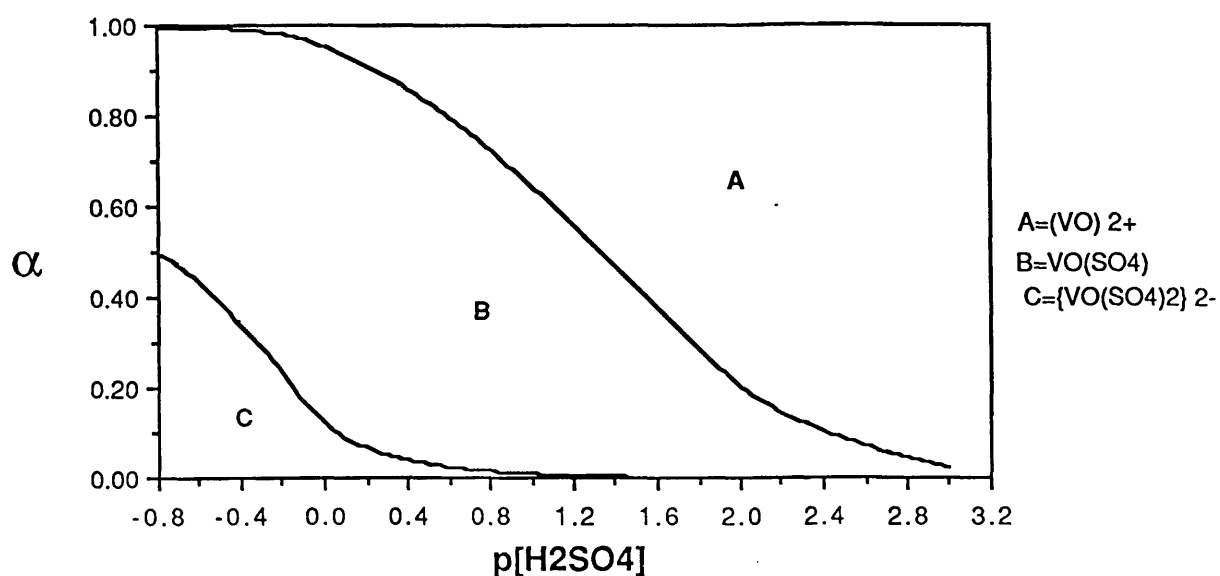


Figure A12 Stability field diagram for the complexes formed in the $\text{VO}^{2+}\text{-SO}_4^{2-}$ system.

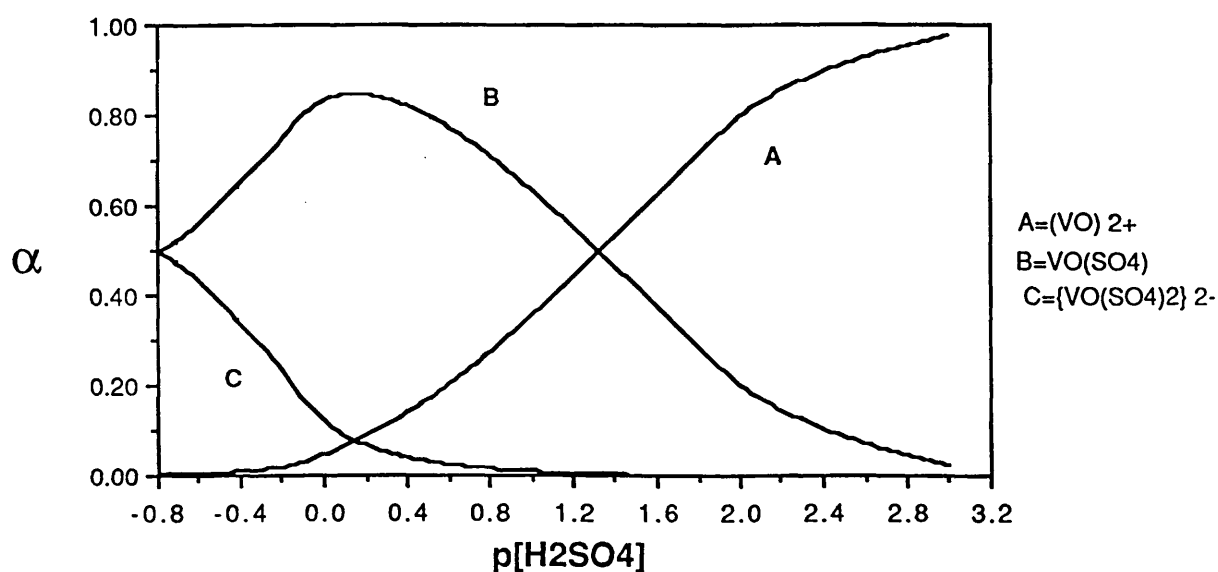


Figure A13 Distribution diagram for the complexes formed in the $\text{VO}^{2+}\text{-SO}_4^{2-}$ system.

A3.2 b) The $\text{VO}^{2+}\text{-HSO}_4^-$ system.

The above calculations can not be repeated for the $\text{VO}^{2+}\text{-HSO}_4^-$ system due to the presence of $\text{VO}^{2+}\text{-SO}_4^{2-}$ complexes which absorb at the same wavelength and sulphuric acid concentration range as the $\text{VO}^{2+}\text{-HSO}_4^-$ complexes. The increase in absorbance in the 450 to 500nm wavelength range at sulphuric acid concentrations greater than 8 M can certainly be assigned to a bisulphate complex, but it is not possible to calculate from the available data whether this is the first or the fifth stepwise complex, or whether dimerization is taking place. Thus, no further calculations will be made.

A4 DISCUSSION.

The calculated K_1 values for the systems studied showed very large standard deviations. The reason for this is best illustrated with an example. Consider the $\text{VO}^{2+}\text{-SO}_4^{2-}$ system; the absorbance values at a wavelength of 630nm for 0 and 1 M sulphuric acid solutions were 0.0824 and 0.0840, respectively, for a vanadium concentration of 1.5×10^{-2} M. The error of the absorbance readings was estimated to be ± 0.0005 . To calculate K_1 the values of $1/(\epsilon^\lambda - \epsilon_0^\lambda)$ are required, and from Beer's law these are proportional to $1/(A^\lambda - A_0^\lambda)$, where A is the absorbance. Taking due account of the error, the following range of values for $(A^\lambda - A_0^\lambda)$ are obtained:

$$0.0835 - 0.0819 = 0.0016$$

$$0.0835 - 0.0829 = 0.0006$$

$$0.0845 - 0.0819 = 0.0026$$

$$0.0845 - 0.0829 = 0.0016$$

Thus, the range in $(A^\lambda - A_0^\lambda)$ is 0.0006 to 0.0026. There is not only a large difference between these values but the lower limit is very close to the error value (even though errors arising from

metal concentration, acid preparation, glassware, etc., have been ignored). Therefore, the large standard deviation in K_1 is due to limits in the accuracy of the instrument, and to reduce it an instrument at least ten times more accurate would be required. Further proof of lack of sufficient accuracy in the instrument lies in Figure A9, where two lines cross in three positions, but other lines fail to cross these same points (thus, these are not isobestic points).

Figures A2 and A9 show that there is little change in the shape of the absorption spectra for both VO_2^+ and VO^{2+} as the sulphuric acid concentration rises. From these data it can be inferred that no change takes place in the structure of the complexes with increasing acid concentration. Mishra and Symons [110] suggested the formation of a five coordination complex for vanadium (V) in 100% sulphuric acid (reactions A1 and A2) based on the similarity between the UV spectra for this and VOCl_3 . Quinquevalent vanadium forms two oxo-species VO^{3+} and VO_2^+ [117]. The former is found in oxyhalides, and it appears to form complexes with five or six coordinated monomers of the form $\text{VOCl}_3 \cdot \text{L}$ and $\text{VOCl}_3 \cdot 2\text{L}$, where L is an oxygen or nitrogen donor ligand. The structure of the second species, VO_2^+ , is less well characterized. The solid $\text{VO}_2(\text{NO}_3)$ has been prepared, and its infrared spectrum is consistent with the presence of ionic nitrate and with a $\text{V}=\text{O}$ bond. Similar results have been obtained for the compounds VO_2F and $\text{VO}_2(\text{SbF}_6)$ [117]. In strongly acidified vanadium (V) solutions the VO_2^+ ion, probably $[\text{VO}_2(\text{H}_2\text{O})_4]^+$, is formed. It is known to complex when anions other than ClO_4^- and CF_3SO_3^- are present; for example in HCl the anion is *cis*- $[\text{VO}_2\text{Cl}_4]^{3-}$. There are other anions such as *cis*- $[\text{VO}_2\text{EDTA}]^{3-}$ and *cis*- $[\text{VO}_2(\text{C}_2\text{O}_4)_2]^{3-}$. All such species have *cis*-dioxo groups, and they give band in infrared and raman spectra characteristic for $\text{V}=\text{O}$ groups. The *cis* arrangement for dioxo compounds of metals with no d electrons is preferred over the *trans* arrangement because there is greater share of the atomic orbitals [121]. The cation VO_2^+ is considered to be bent with C_{2v} symmetry [117].

Thus, the $\text{VO}_2(\text{HSO}_4)_n^{-n+2}$ complexes are believed to have an octahedral structure, with VO_2^+ ion retaining the C_{2v} symmetry. As with other VO_2^+ complexes the maximum coordination number is probably four giving rise to the $\text{VO}_2(\text{HSO}_4)_4^{-2}$ at high sulphuric acid concentrations. The maximum coordination number may not have been achieved in this case because of dimerization of the complexes. The only change occurring as the sulphuric acid concentration increases (up to about 12 M) is that H_2O molecules are replaced by HSO_4^- ions. These complexes are weak and there is little interaction between the central cation and the ligands as shown by the low values of the stepwise stability constants. The sulphate and bisulphate ligands are generally very similar, and according to Wilkinson [135] there no theoretical reason why the sulphate ion should not have complexed with the VO_2^+ ion.

As already mentioned in Section A1, in acid solutions the vanadium (IV) species is the $[\text{VO}(\text{H}_2\text{O})_5]^{2+}$ ion, which has a distorted octahedral structure with the water molecule trans to the oxygen being less strongly bonded than the equatorial waters. This structure is probably retained as the SO_4^{2-} and HSO_4^- ions replace the water molecules. However, it is possible that because of the larger size of these ions the structure might change to a five-coordination square pyramid. Examples of such complexes exist such as $[\text{VO}(\text{bipy})_2\text{Cl}]^+$ (bipy=2,2-dipyridine); however, a number of VO^{2+} five-coordinate complexes are known to add ligands thus becoming octahedral [121].

No mixed complexes, such as $\text{VO}(\text{HSO}_4)_n(\text{SO}_4)_m$, were considered because of lack of sufficient information. The stepwise stability constants of the VO^{2+} -sulphate complexes were calculated on the assumption that they were more stable than the VO^{2+} -bisulphate complexes; this assumption is based on the fact that sulphate is almost certainly acting as a bidentate ligand, and increase stability is achieved through the chelate effect.

APPENDIX B.

TWO-PHASE FLUIDIZED BED MODEL.

A two-phase, bubble-emulsion model was applied to the behaviour of the fluidized bed. The parameters of the model were estimated using equations B1 to B24; these equations are derived and explained by Kunii and Levenspiel [129] and Davidson and Harrison [130]. A list of symbols is given in Appendix C.

The two-phase fluidization model assumes:

- a) All particles are in the dense phase, which occupies a fraction $(1-\delta)$ of the bed, which itself has a void fraction ϵ_{mf} and where the interstitial gas velocity is (u_{mf}/ϵ_{mf}) .
- b) The fluid in the dense phase is considered to be in plug flow.
- c) The lean or bubble phase contains no particles and is in plug flow with absolute velocity u_B (in reality a fraction of about 0.1-1% of the solids is present in the bubble phase).

The superficial velocity of fluidizing gas, u_0 , is given by:

$$u_0 = \delta u_B + (1-\delta)u_{mf} \quad (B1)$$

where u_{mf} is the minimum fluidization velocity, u_B is the bubble velocity, and δ is the volume fraction of gas bubbles, which is defined by:

$$\delta = 1 - \frac{L_{mf}}{L_f} \quad (B2)$$

where L_{mf} is the depth of the fluidized bed at u_{mf} and L_f is the

bed depth at u_0 . The void fraction, ϵ_f , of a fluidized bed can be calculated by:

$$\epsilon_f = 1 - \frac{L_{mf}(1-\epsilon_{mf})}{L_f} \quad (B3)$$

The bubble diameter, d_B , and the bubble velocity, u_B , in a fluidized bed are given by equations B4 and B5 below.

$$d_B = \frac{1}{g} \left[\frac{L_{mf}}{L_f - L_{mf}} \frac{u_0 - u_{mf}}{0.711} \right]^2 \quad (B4)$$

$$u_B = u_0 - u_{mf} + 0.711(gd_B)^{1/2} \quad (B5)$$

u_0 is further defined by:

$$u_0 = u_{20} \frac{T}{293} \quad (B6)$$

where u_{20} is the superficial gas velocity at 20°C and T is the absolute temperature of the experiment.

The self diffusivity of hydrogen chloride gas, D , in nitrogen is given by [141]:

$$D = \frac{B T^{3/2} \sqrt{1/M_1 + 1/M_2}}{r_{12}^2 I_D P} \quad (B7)$$

where M_1 and M_2 are the molecular mass of HCl and N_2 , respectively; P is the absolute pressure (atm.); I_D is the collision integral for diffusion (function of temperature, at 1000°C for HCl $I_D = 0.3948$); r_{12} is the average molecular

diameters $(=1/2(r_1+r_2))$ for HCl and N_2 , respectively), and B is a constant given by equation B8 below:

$$B = 1 - 2.46 \sqrt{1/M_1 - 1/M_2} \quad (B8)$$

The gas exchange coefficients K_{BE} , K_{BC} and K_{CE} are given by:

Gas bubble-emulsion:

$$\frac{1}{K_{BE}} = \frac{1}{K_{BC}} + \frac{1}{K_{CE}} \quad (B9)$$

Gas bubble-gas cloud:

$$K_{BC} = 4.5 \left[\frac{u_{mf}}{d_B} \right] + 5.85 \left[\frac{D^{1/2} g^{1/4}}{d_B^{5/4}} \right] \quad (B10)$$

Gas cloud-emulsion:

$$K_{CE} = 6.78 \left[\frac{D \epsilon_{mf} u_B}{d_B^3} \right]^{1/2} \quad (B11)$$

In deriving a mass balance for HCl in the fluidized bed it was assumed that the change in gas volume due to the volatilization reactions is negligible, and that the flow rate of the fluidizing gas remained constant along the height of the bed. On the basis of these assumptions expressions can be obtained for the HCl mass balance in the bubble and emulsion phases, equations B12 and B13, respectively:

$$S \delta \epsilon_B \frac{\partial C_B}{\partial t} = -S \delta u_B \frac{\partial C_B}{\partial z} - \frac{N_B}{L_f} 4 \pi r_0^2 k_B C_B - S \delta K_{BE} (C_B - C_E) \quad (B12)$$

$$S(1-\delta)\epsilon_{mf} \frac{\partial C_E}{\partial t} = -S(1-\delta)u_{mf} \frac{\partial C_E}{\partial z} - \frac{N_E}{L_f} 4\pi r_0^2 k_E C_E + S\delta K_{BE}(C_B - C_E) \quad (B13)$$

where S is the cross-sectional area of fluidized bed, ϵ_B is the void fraction of gas bubbles, C_B and C_E are the HCl concentrations in the bubble and emulsion phases; z is the distance from the base of the fluidized bed; N_B and N_E are the number of Flexicoke particles in the bubble and emulsion phases; k_B and k_E are the overall rate constant for bubble and emulsion phases; K_{BE} is the overall gas-exchange coefficient between gas bubbles and emulsion phase. N_B and N_E are given by equations B14 and B15, respectively.

$$N_B = \frac{3SL_f\delta\gamma\psi}{4\pi r_0^3} \quad (B14)$$

$$N_E = \frac{3W}{4\pi r_0^3 \rho_s} - N_B \quad (B15)$$

where γ is the volume fraction of fluidized particles in the bubble phase (assumed to be 0.5%), ψ is percentage of vanadium in the Flexicoke particles, W is the mass of coke fed to the reactor, ρ_s is the density of Flexicoke and r_0 is the mean particle radius.

The solutions to equations B12 and B13 are given by equations B16 and B17, respectively:

$$C_B = \frac{C_0}{(\alpha - \beta)} \left[(\alpha + b + c + d)e^{\alpha z} - (\beta + b + c + d)e^{\beta z} \right] \quad (B16)$$

$$C_E = \frac{C_0}{(\alpha - \beta)} \left[(a + b + \alpha + d)e^{\alpha z} - (a + b + \beta + d)e^{\beta z} \right] \quad (B17)$$

where C_0 is the concentration of HCl at the bottom of the fluidized bed, α and β are the solutions to equation B18 and a , b , c and d are defined by equations B19 to B22, respectively.

$$t_2 + (a + b + c + d)t + (ac + ad + bc) = 0 \quad (B18)$$

$$a = \frac{4\pi r_0^2 N_B k_B}{S \delta u_B L_f} \quad (B19)$$

$$b = \frac{K_{BE}}{u_B} \quad (B20)$$

$$c = \frac{4\pi r_0^2 N_E k_E}{S(1 - \delta) u_{mf} L_f} \quad (B21)$$

$$d = \frac{\delta K_{BE}}{(1 - \delta) u_{mf}} \quad (B22)$$

By integrating equations B16 and B17 with respect to z , the average concentration of HCl in the bubble and emulsion phases C_{B_0} and C_{E_0} , respectively, can be found.

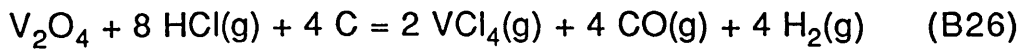
$$C_{B_0} = \frac{C_0}{L_f(\alpha - \beta)} \left[\left[\frac{\alpha + b + c + d}{\alpha} \right] (e^{\alpha L_f} - 1) - \left[\frac{\beta + b + c + d}{\beta} \right] (e^{\beta L_f} - 1) \right] \quad (B23)$$

$$C_{E_0} = \frac{C_0}{L_f(\alpha - \beta)} \left[\left[\frac{a + b + \alpha + d}{\alpha} \right] (e^{\alpha L_f} - 1) - \left[\frac{a + b + \beta + d}{\beta} \right] (e^{\beta L_f} - 1) \right] \quad (B24)$$

To calculate the average concentrations of HCl the overall rate constants in the bubble and emulsion phase were assumed to be equal, thus, $k_B = K_E = K'$. At 1000°C and with pure HCl the experimental vanadium extraction rate, k_V , using equation B25 was found to be $5.93 \times 10^{-4}/\text{sec}$.

$$R_t = R_{\max} \{1 - \exp(K_V t)\} \quad (\text{B25})$$

For the reaction:



the rate of HCl consumption is four times the rate of vanadium extraction; the moles of V_2O_4 extracted from Flexicoke, Q_V , are given by:

$$Q_V = \frac{W_V R_{\max}}{M_{\text{V}_2\text{O}_4}} \quad (\text{B27})$$

where $M_{\text{V}_2\text{O}_4}$ is the atomic mass of V_2O_4 , ψ is the concentration of vanadium in Flexicoke and $R_{\max}$ is the maximum vanadium extraction (55%). Therefore, the rate of HCl consumption, k' , is given by $k' = 4K_V Q_V$, which was calculated to be $3.2 \times 10^{-6} \text{ mol/sec}$.

Table B1 below gives the value to a number of parameters required to calculate the HCl concentration profile in the fluidized bed. The density HCl was obtained from the literature [140]; the other values were measured in the fluidized bed, at 20°C.

Density of Flexicoke (at 20°C), Kg/m ³	1440
Density of HCl (at 20°C), Kg/m ³	1.2
Average particle diameter, m	1.38x10 ⁻⁴
ϵ_{mf}	0.46
u_{mf} (at 20°C), m/sec	6.6x10 ⁻³
S, m ²	7.07x10 ⁻⁴
Terminal velocity, m/sec	7.4x10 ⁻²
L_{mf} , m	5.5x10 ⁻²
C_0 (at 1000°C), mol/m ³	9.57

Table B1 Some physical parameters associated with a fluidized bed of Flexicoke.

Figures B1 and B2 give the HCl concentration profiles for the bubble and emulsion phase, respectively, for the flow rates used in Figure 5.33. Table B2 below gives a number of the parameters from the mass balance calculations at various HCl flow rates.

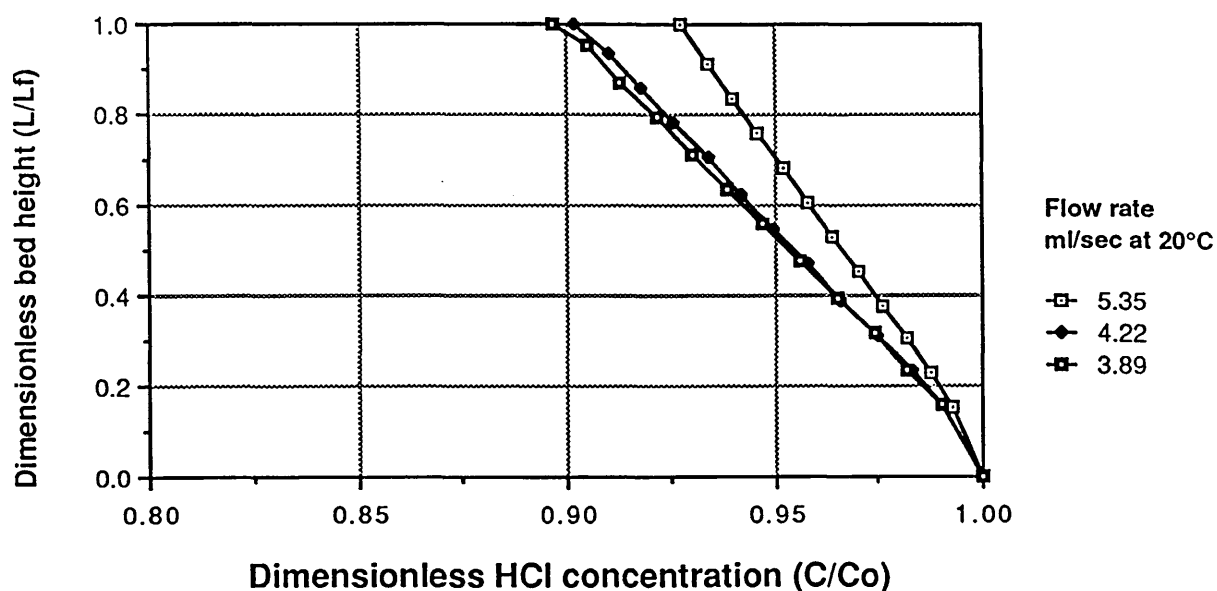


Figure B1 HCl concentration profiles in the bubble phase; HCl partial pressure=1.0, temperature=1000°C.

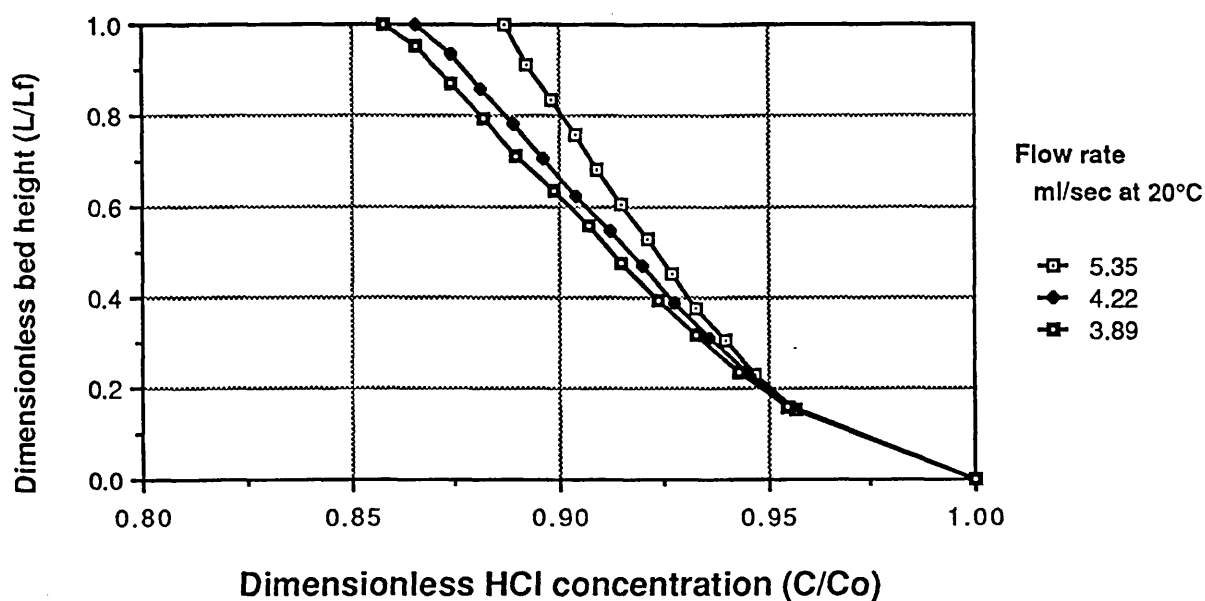


Figure B2 HCl concentration profiles in the emulsion phase; HCl partial pressure=1.0, temperature=1000°C.

Calculated parameters	Gas flow rate, ml/sec at 20°C		
	3.89	4.22	5.35
δ	0.13	0.15	0.17
ε_f	0.53	0.54	0.55
L_f , m	6.3×10^{-2}	6.4×10^{-2}	6.6×10^{-2}
d_B , m	2.483×10^{-3}	2.480×10^{-3}	3.127×10^{-3}
u_B , m/s	0.128	0.130	0.151
D , m^2/s	3.01×10^{-7}	3.01×10^{-7}	3.01×10^{-7}
K_{BC} , s^{-1}	22.21	22.23	17.18
K_{CE} , s^{-1}	7.31	7.37	5.60
K_{BE} , s^{-1}	5.50	5.54	4.23
C_{B_0}/C_0	0.964	0.964	0.974
C_{E_0}/C_0	0.916	0.920	0.927

Table B2 Theoretically determined parameters for fluidized bed at various HCl flow rates.

The concentration profiles are time dependent, and those given in Figures B1 and B2 show the HCl concentration when vanadium is extracted at the maximum rate. Thus, these figures represent the HCl available for reaction with the nickel values in Flexicoke. From this it can be seen that there is an excess of HCl gas in both the bubble and emulsion phase at all flow rates considered and thus HCl depletion cannot be the reason for the induction time effect observed for nickel extraction.

APPENDIX C.

LIST OF SYMBOLS.

a	Composite parameter used to solve equation B16 and B17.
b	Composite parameter used to solve equation B16 and B17.
B	Constant given by equation B8.
c	Composite parameter used to solve equation B16 and B17.
C	Leachant concentration.
C	Total vanadium concentration (Appendix A).
C_B	HCl concentration in the bubble phases.
C_E	HCl concentration in the emulsion phases.
C_0	HCl concentration at the bottom of the fluidized bed.
C_{B0}	Average concentration of HCl in the bubble phase.
C_{E0}	Average concentration of HCl in the emulsion phase.
d	Composite parameter used to solve equation B16 and B17.
d_B	Bubble diameter.
D	Self diffusivity of hydrogen chloride gas.
D_E	Effective diffusion coefficient.
g	Acceleration due to gravity.
I_D	Collision integral for diffusion.
k'	Overall rate constant.
k_B	Overall rate constant for bubble phases.
k_E	Overall rate constant for emulsion phases.
k_V	Vanadium extraction rate from Flexicoke in fluidized reactor.
K_{BE}	Gas bubble-emulsion phase gas exchange coefficient.
K_{BC}	Gas bubble-gas cloud gas exchange coefficient.
K_{CE}	Gas cloud-emulsion phase gas exchange coefficient .
K_n	Stepwise stability constant for complex n.
L_f	Depth of fluidized bed.
L_{mf}	Depth of the fluidized bed at the minimum fluidization velocity.
M	Molecular mass.
N_B	Number of Flexicoke particles in the bubble phase.
N_E	Number of Flexicoke particles in the emulsion phase.
P	Absolute pressure, atm.
$p[H_2SO_4]$	$-\log(\text{Sulphuric acid concentration, M})$.
Q_V	Moles of V_2O_4 extracted from Flexicoke.

r_0	Average radius of Flexicoke particle.
r_{12}	Average molecular radius.
$R_{\max}$	Maximum vanadium extraction in a fluidized vapour transport experiment.
R_t	Vanadium extraction at time t in a fluidized vapour transport experiment.
S	Cross-sectional area of fluidized bed.
t	Time.
T	Absolute temperature, K.
u_B	Bubble velocity.
u_{mf}	Minimum fluidization velocity.
u_0	Superficial velocity of fluidizing gas.
u_{20}	Superficial gas velocity at 20°C.
V_m	Molecular volume of vanadium (IV) oxide.
W	Mass of coke fed to the reactor.
z	Distance from the base of the fluidized bed.

Greek.

α	Solution (with β) to equation B18.
α	Fraction of vanadium extracted into solution.
α_n	Fraction of complex n in solution.
β	Solution (with α) to equation B18.
β_n	Overall stability constant for complex n .
γ	Volume fraction of fluidized particles in the bubble phase
δ	Volume fraction of gas bubbles.
ϵ_B	Void fraction of gas bubbles.
ϵ_f	Void fraction of a fluidized bed.
ϵ_{mf}	Void fraction of a fluidized bed at minimum fluidization flow rate.
ϵ^λ	Overall molar absorption coefficient.
ϵ_n^λ	Molar absorption coefficient for stepwise complex n .
λ	Wavelength, nm.
ρ_s	Density of Flexicoke.
σ	Standard deviation.
σ	Stoichiometric factor.
θ_n	Constant to evaluate standard deviation of β_n .
ψ	Vanadium concentration in Flexicoke particles.

**APPENDIX D
DATA TABLES**

Time (min)	Temperature (°C)				
	30	40	50	60	70
0	0.0	0.0	0.0	0.0	0.0
5	23.7	38.3	39.2	48.9	58.5
10	37.3	44.6	46.0	55.2	66.7
15	42.9	48.5	55.4	62.0	-
30	51.9	60.0	61.8	66.4	76.4
60	-	69.5	71.4	72.4	76.8
90	65.0	73.1	75.4	-	77.8
120	69.3	74.1	75.5	-	78.8
180	71.0	74.3	-	77.9	-

Table D1 Effect of temperature on the vanadium extraction from ground Flexicoke.

-53 μ m ground Flexicoke, 1M sulphuric acid, 550 rpm agitation speed

Time (min)	Sulphuric acid concentration (M)						
	0.25	0.5	1.0	1.5	2.5	4.0	6.0
0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1	32.9	-	-	27.3	20.5	25.9	-
3	35.2	-	-	32.3	24.9	27.0	17.6
5	38.3	28.4	38.3	36.2	27.5	28.1	17.7
10	42.0	40.2	44.6	38.7	29.9	28.5	19.6
15	44.6	47.5	48.5	41.6	30.0	33.0	20.7
30	54.5	53.9	60.0	49.4	33.5	40.2	23.8
45	59.7	-	-	58.8	35.2	42.9	26.5
60	62.7	64.0	69.5	63.8	39.5	44.4	28.4
90	64.3	72.3	73.1	71.2	46.8	45.6	34.5
120	66.2	-	74.1	-	51.2	50.0	36.3
135	-	-	-	74.7	-	-	-

Table D2 Effect of sulphuric acid concentration on the vanadium extraction from ground Flexicoke.

-53 μ m ground Flexicoke, temperature = 40°C, 550 rpm agitation speed

Time (min)	Agitation speed (rpm)			Time (min)	Size fraction of ground Flexicoke (μm)		
	550	900	1200		-53+45	-75+53	-106+75
0	0.0	0.0	0.0	0	0.0	0.0	0.0
1	-	20.5	21.0	1	18.3	15.7	5.4
5	38.3	35.6	32.0	3	31.7	21.2	6.8
10	44.6	45.6	39.7	5	38.5	27.3	7.6
15	48.5	48.8	52.3	10	51.0	32.4	9.2
30	60.0	59.0	57.1	15	54.0	37.4	10.3
45	69.5	65.3	64.6	30	61.2	41.4	12.3
60	73.1	-	-	60	66.1	43.6	15.3
75	-	72.2	70.0	120	69.4	46.4	17.9
90	74.1	72.3	75.0	180	74.1	48.0	18.3

Table D3 Effect of agitation speed and coke particle size on the vanadium extraction from ground Flexicoke.

Agitation data=-53 μm ground Flexicoke, temperature = 40°C, 1M sulphuric acid.

Particle size data = 1M sulphuric acid, temperature=40°C, 550 rpm agitation speed

Time (min)	Temperature ($^{\circ}\text{C}$)			
	30	50	70	90
0	0.0	0.0	0.0	0.0
5	3.1	3.0	3.4	4.3
10	3.6	3.7	3.5	4.6
15	3.9	4.1	3.7	4.9
30	3.9	4.2	3.9	5.5
60	4.9	4.7	5.2	5.8
150	5.0	5.3	5.4	7.1
225	-	5.7	6.7	7.3

Table D4 Effect of temperature on the vanadium extraction from as-received Flexicoke

As-received Flexicoke, 1M sulphuric acid, 550 rpm agitation speed

Time (days)	Leachant		
	1M HCl/0.1M Fe(3)	1M NaOH	1M H ₂ SO ₄
0	0.0	0.0	0.0
0.042	9.3	6.1	5.9
0.2	11.9	9.3	7.5
1	12.3	12.7	8.5
2	12.4	12.8	11.6
3	12.4	12.9	-
4	12.6	12.9	12.5
5	13.0	13.0	12.6
6	14.1	-	12.9

Table D5 Effect of leachant on the vanadium extraction from as-received Flexicoke.

As-received Flexicoke, temperature =80°C, 550 rpm agitation speed.

Time (min)	Treatment code							
	[1]	a	b	ab	c	ac	bc	abc
0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
5	2.1	5.4	6.1	7.4	4.1	4.7	11.7	9.0
10	3.2	11.6	14.7	15.6	8.7	9.4	23.1	18.5
15	5.2	18.2	21.8	20.1	12.6	13.4	32.1	21.2
30	7.2	25.8	28.4	37.9	15.9	16.6	39.6	38.0
45	9.9	33.0	33.0	44.6	19.5	19.5	45.6	45.2
60	16.2	40.9	37.5	46.9	23.8	22.0	47.9	47.2
90	24.1	46.0	40.2	50.1	28.5	24.0	50.1	50.6
120	32.9	50.0	42.2	53.9	33.1	25.6	52.7	53.3
180	42.8	50.0	43.3	52.9	38.2	27.5	53.6	52.9

Table D6 Vanadium extractions from factorial design 3.

Time (min)	Treatment code							
	[1]	a	b	ab	c	ac	bc	abc
0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
5	0.0	2.8	0.0	2.7	6.6	1.6	0.0	3.0
10	0.2	4.5	3.8	4.4	8.3	3.8	8.6	6.6
15	0.3	5.4	7.0	9.3	9.5	5.5	14.0	15.2
30	0.6	6.1	11.4	15.4	11.2	8.8	21.7	25.5
45	0.5	7.2	16.7	23.7	15.2	13.3	29.6	37.3
60	1.7	9.2	23.9	35.2	19.7	19.7	35.9	50.9
90	2.7	13.5	31.5	47.7	25.5	29.1	43.2	61.8
120	4.8	17.3	39.0	61.9	28.7	37.0	51.2	72.2
180	6.0	28.7	47.5	73.4	30.6	54.6	54.4	80.0

Table D7 Nickel extractions from factorial design 3.

Time (min)	Temperature (°C)				
	1000	950	900	800	700
0	0.0	0.0	0.0	0.0	0.0
5	9.0	2.6	11.7	16.9	2.6
10	18.5	11.2	23.1	16.9	8.6
15	21.2	30.0	32.1	21.5	13.6
30	38.0	46.7	39.6	22.0	15.2
45	45.2	47.0	45.6	22.2	16.6
60	47.2	55.3	47.9	23.4	21.0
79	-	55.7	-	-	-
90	50.6	-	50.1	23.7	21.6
120	53.3	59.8	52.7	31.0	24.2
180	52.9	61.1	53.6	32.3	34.5

Table D8 Effect of temperature on the vanadium extraction from as-received Flexicoke.

As-received (-180µm) Flexicoke, HCl partial pressure=1.0, flow rate ratio=3.0

Time (min)	Temperature (°C)				
	1000	950	900	800	700
0	0.0	0.0	0.0	0.0	0.0
5	4.7	2.4	4.1	2.4	2.5
10	9.4	7.3	8.7	3.6	3.3
15	13.4	7.2	12.6	7.1	4.1
30	16.6	15.9	15.9	8.6	6.0
45	19.5	19.8	19.5	11.8	7.0
60	22.0	27.0	23.8	18.8	9.6
90	24.0	46.4	28.5	-	16.8
120	25.6	46.9	33.1	20.7	-
180	27.5	52.1	38.2	-	16.8
220	-	-	-	26.3	16.9

Table D9 Effect of temperature on the vanadium extraction from as-received Flexicoke.

As-received (-180 μ m) Flexicoke, HCl partial pressure=0.25, flow rate ratio=3.0

Time (min)	HCl partial pressure				
	1	0.5	0.25	0.05	0.01
0	0.0	0.0	0.0	0.0	0.0
5	9.0	11.8	4.7	-	-
10	18.5	18.4	9.4	2.1	2.5
15	21.2	22.2	13.4	-	-
20	-	-	-	5.6	-
30	38.0	29.5	16.6	5.7	3.3
45	45.2	30.0	19.5	6.5	3.6
60	47.2	30.1	22.0	8.5	4.7
90	50.6	32.4	24.0	14.6	-
120	53.3	-	25.6	18.3	5.2
180	52.9	40.0	27.5	37.7	10.2
200	-	-	-	-	11.4
248	-	41.0	-	-	-
300	-	-	-	-	18.1
360	-	-	-	-	20.8

Table D10 Effect of HCl partial pressure on the vanadium extraction from as-received Flexicoke

As-received (-180 μ m) Flexicoke, 1000°C, flow rate ratio=3.0

Time (min)	HCl partial pressure				
	1	0.5	0.25	0.05	0.01
0	0.0	0.0	0.0	0.0	0.0
5	11.7	3.9	4.1	-	-
10	23.1	6.0	8.7	-	1.7
15	32.1	20.4	12.6	-	-
22	-	-	-	1.2	-
30	39.6	26.9	15.9	1.9	3.1
45	45.6	27.2	19.5	2.9	4.4
60	47.9	27.9	23.8	4.8	-
72	-	-	-	6.8	5.5
90	50.1	30.3	28.5	-	-
120	52.7	33.2	33.1	8.7	6.8
171	-	37.7	-	11.7	-
180	53.6	-	38.2	-	7.5
245	-	-	-	12.8	7.7
307	-	-	-	-	14.5
398	-	-	-	-	25.2

Table D11 Effect of HCl partial pressure on the vanadium extraction from as-received Flexicoke

As-received (-180 μ m) Flexicoke, 900°C, flow rate ratio=3.0

Time (min)	Temperature (°C)				
	1000	950	900	800	700
0	0.0	0.0	0.0	0.0	0.0
5	3.0	1.5	0.0	3.8	2.6
10	6.6	11.6	8.6	8.3	6.3
15	15.2	16.6	14.0	8.6	6.9
30	25.5	22.3	21.7	10.8	7.2
45	37.3	32.7	29.6	11.6	7.3
60	50.9	56.8	35.9	13.4	7.5
79	-	58.6	-	-	-
90	61.8	-	43.2	16.2	8.1
120	72.2	69.7	51.2	19.9	13.8
180	80.0	76.8	54.4	20.9	18.5

Table D12 Effect of temperature on the nickel extraction from as-received Flexicoke.

As-received (-180 μ m) Flexicoke, HCl partial pressure=1.0, flow rate ratio=3.0

Time (min)	Temperature (°C)				
	1000	950	900	800	700
0	0.0	0.0	0.0	0.0	0.0
5	1.6	1.5	6.6	0.4	1.8
10	3.8	1.5	8.3	0.4	2.4
15	5.5	6.5	9.5	1.7	4.9
30	8.8	8.5	11.2	4.1	5.0
45	13.3	9.2	15.2	4.6	5.4
60	19.7	9.3	19.7	10.0	5.4
90	29.1	31.6	25.5	10.0	7.9
120	37.0	33.3	28.7	-	-
180	54.6	46.7	30.6	11.5	12.2
220	-	-	-	-	13.1

Table D13 Effect of temperature on the nickel extraction from as-received Flexicoke.

As-received (-180 μ m) Flexicoke, HCl partial pressure=0.25, flow rate ratio=3.0

Time (min)	HCl partial pressure				
	1	0.5	0.25	0.05	0.01
0	0.0	0.0	0.0	0.0	0.0
5	3.0	3.7	1.6	-	-
10	6.6	6.9	3.8	0.0	0.1
15	15.2	12.4	5.5	-	-
30	25.5	25.2	8.8	1.5	2.3
45	37.3	33.6	13.3	3.2	2.4
60	50.9	40.9	19.7	6.9	2.7
90	61.8	58.6	29.1	11.7	-
120	72.2	-	37.0	19.9	3.3
180	80.0	76.6	54.6	24.6	6.1
248	-	79.6	-	55.9	14.3
300	-	-	-	-	15.6
360	-	-	-	-	20.5

Table D14 Effect of HCl partial pressure on the nickel extraction from as-received Flexicoke.

As-received Flexicoke (-180 μ m), 1000°C, flow rate ratio=3.0

Time (min)	HCl partial pressure				
	1	0.5	0.25	0.05	0.01
0	0.0	0.0	0.0	0.0	0.0
5	0.0	2.2	6.6	-	-
10	8.6	7.9	8.3	1.5	0.3
15	14.0	13.9	9.5	-	-
22	-	-	-	4.7	-
30	21.7	20.1	11.2	5.4	1.6
45	29.6	24.5	15.2	7.8	2.3
60	35.9	29.8	19.7	8.2	-
72	-	-	-	-	4.7
90	43.2	32.1	25.5	11.0	-
120	51.2	38.4	28.7	14.0	7.1
171	-	45.0	-	-	-
180	54.4	-	30.6	15.2	7.2
245	-	-	-	18.8	8.2
307	-	-	-	-	11.9
398	-	-	-	-	20.5

Table D15 Effect of HCl partial pressure on the nickel extraction from as-received Flexicoke

As-received (-180 μ m) Flexicoke, 900°C, flow rate ratio=3.0

Time (min)	HCl partial pressure							
	1		0.75		0.5		0.25	
	V	Ni	V	Ni	V	Ni	V	Ni
0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
5	9.8	0.0	-	-	-	0.0	-	0.0
10	27.5	0.0	19.3	0.5	5.5	0.0	5.3	0.0
15	40.5	0.0	29.7	1.6	12.8	0.0	7.6	0.0
30	49.7	1.8	44.0	0.0	18.8	1.0	10.3	1.0
45	59.4	3.0	54.8	4.5	27.0	1.0	12.9	-
60	67.1	8.0	61.6	9.1	40.3	8.3	15.5	-
90	72.1	17.1	68.6	10.6	52.4	11.2	22.3	3.1
120	73.3	39.9	71.5	29.7	67.7	14.7	30.0	3.5
180	74.3	68.8	74.0	39.0	70.9	26.0	42.9	6.8

Table D16 Effect of HCl partial pressure on the vanadium and nickel extractions from ground Flexicoke

-90+75 μ m ground Flexicoke, 1000°C, flowrate ratio=3.0

Acid concentration (g/l)	Mass of vanadium (V) oxide dissolved (g/l)	Mass of vanadium (IV) sulphate dissolved (g/l)
50	11.9	537.6
100	17.9	534.4
200	27.5	384.0
300	28.5	348.8
500	30.0	317.6
800	32.1	26.0
1000	47.8	18.6
1300	37.9	2.5
1700	0.8	1.1

Table D17 Effect of Sulphuric acid concentration on the solubility of vanadium (V) oxide and vanadium (IV) sulphate at 25°C.

Time (min)	Particle size fraction					
	-106+90µm		-90+75µm		-75+53µm	
	V	Ni	V	Ni	V	Ni
0	0	0	0	0	0	0
5	8.6	2.35	9.84	0	10	0
10	18.4	4	27.46	0	17.612	0
15	30.6	6.6	40.47	0	28.208	1.9
30	45.9	10.14	49.66	1.81	47.112	2.4
45	59.2	18.57	59.44	2.96	56.444	3.4
60	62	31.46	67.09	7.97	65.432	8.9
90	72.2	51.16	72.07	17.1	76.66	20.21
120	75.2	62.43	73.31	39.85	77	21.9
180	77.5	74.84	74.3	68.8	77.3	32.7

Table D18 Effect of particle size on the vanadium and nickel extraction from ground Flexicoke.

Temperature=1000°C, HCl partial pressure=1.0, flow rate ratio=3.0

REFERENCES

1. Yen T.F. *Chemical aspects of metals in native petroleum*. Chapter 1. *The role of trace metals in petroleum*. Yen T.F. (Ed), Ann Arbor, Michigan, 1975, 221 pp.
2. Sugihara J.M. *Trace metal constituents in petroleum*. American Petroleum Institute, Division of Science and Technology, **42** (8), 1962, 30-32.
3. Woodle R.A. and Chandler W.B., *Industrial and Engineering Chemistry*, **44**, 1952, 2591.
4. Hodgson G.W., Baker B.L. and Peake E., *The role of porphyrins in the geochemistry of petroleum*, *Proceedings 7th World Petroleum Congress, Mexico*, **9**, 1967, 117-128.
5. Skinner D.A. *Chemical state of Santa Maria Valley crude oil*, *Industrial and Engineering Chemistry*, **44** (5), 1952, 1159-1165.
6. Dunning H.N. and Moore J.W. *Properties of porphyrins in petroleum*, *Industrial and Engineering Chemistry*, **46** (9), 1954, 2000-2007.
7. Beach L.W. and Shewmaker J.E. *The nature of vanadium in petroleum*, *Industrial and Engineering Chemistry*, **49** (7), 1957, 1157-1164.
8. Theibs A., *Ann. der Chem.*, **510**, 1934, 42-62.
9. Speight J.G. and Moschopedis S.E. *On the molecular nature of petroleum asphaltene from Chemistry of Asphaltenes*, *Advances in Chemistry Series 195*, American Chemical Society, Washington, 1981, 260 pp.

10. Tilby R.H. *The nature of metals in petroleum*. Chapter 2. *The role of trace metals in petroleum*. Yen T.F. (Ed), Ann Arbor, Michigan, 1975, 221pp.
11. Hodgson G.W., Bulletin of the American Association of Petroleum Geologists, **38**, 1954, 2200.
12. Hyden H.J., US Geological Survey Bulletin, 1961, 1100-B.
13. Scott J., Collins G.A. and Hodgson G.W., Canadian Mining and Metallurgical Bulletin., **47**, 1954, 36.
14. Garner F.H., Green S.J., Harper F.D. and Pegg R.E., Journal of the Institute of Petroleum, **39**, 1953, 1159.
15. Hodgson G.W. and Baker B.L. Bulletin of the American Association of Petroleum Geologists, **43**, 1959, 311.
16. Speight J.G. *The chemistry and technology of petroleum*, Marcel Dekker Inc., New York, 1980, 498 pp.
17. Garcia L. *The refining strategy of petroleum with high metal contents*. Proceedings International symposium of vanadium and other metals in petroleum, Paper K, Section IV, Maracaibo, Venezuela, 1973.
18. De Biase R. and Elliot J.D. *Delayed coking: latest trends*, Hydrocarbon processing, **61**(5), 1982, 99-104.
19. Gary J.H. and Handwerk G.E. *Petroleum refining, technology and economics*, Marcel Dekker Inc., New York, 1975, 365 pp.
20. Tomas J.J. and Pinzon P. *A technical and economic evaluation of coking processes for heavy oil upgrading*, Proceedings III International Seminar Intevep, *Usos alternos del coque*, Calderon J.L. and Hernandez M. (Eds.), Intevep, Caracas, 1982, 131 pp.

21. Jansen H.R. *Getting maximum value from residual oil through Delayed coking*, *Ibid*, 19-29.
22. Di Elsi D.P., Miller D.J. and Cox N.R. *Modern Delayed coker pilot plant*, *Energy progress*, **3** (4), 1983, 193-196.
23. Metrailer W.J., Royle R.C. and Lahn G.C. *Properties of cokes produced by the Flexicoking process from Petroleum derived carbons*, American Chemical Society, Symposium Series 21, Deviney M.L. and O'Grady T.M. (Eds), Washington, 1976, 463 pp
24. Anon. *Coking process offers great flexibility*, *Chemical and Engineering News*, **52**(48), 1974, 17-18.
25. Matula J.P., Molstedt B.V. and Ryan D.F. *Flexicoker prototype demonstrates successful operation*, American Petroleum Institute, Proceedings Division of Refining, 1975, 227-242.
26. Griffel J., Phillips G.E. and Spry J.C. *Flexicoking clean products from dirty feeds*, American Petroleum Institute, Proceedings Division of Refining, 1976, 673-694.
27. Matula J.P., Weinberg H.N. and Weissman W. *Sour crudes target for new coking process*, *Oil and Gas Journal*, **70**(38), 1972, 67-71. Based on paper presented at 37th mid-year meeting of American Petroleum Institute, Proceedings Division of Refining, 1972.
28. Allen D.E., Metrailer W.J. and King R.C. *Advances in Fluid and Flexicoking technology*, *Chemical Engineering Progress*, **77**(12), 1981, 40-44.
29. Allen D.E., Say G.R., Heinzelmann F.J. and Lowenthal S.S. *New developments enhance attractiveness of Flexicoking technology*, American Petroleum Institute, Proceedings Division of Refining, 1982, 221-227.

30. Allen D.E., Blaser D.E. and Lambert M.M. *Dual-gasification coking process offers option for synthesis gas production from heavy feeds*. Oil and Gas Journal, **80**, May 17, 1982, 93-102.
31. Valkovic V. *Trace metals in petroleum*, PPC Books, Tuba, Oklahoma, 1978, 269 pp.
32. Jones P. *Trace metals and other elements in crude oils: a literature review*, British Petroleum Co., Sudbury, 1975, 40 pp.
33. Babu S.P. (Ed). *Trace elements in fuel*, Symposium Division of Fuel chemistry, American Chemical Society, Advances in Chemistry Series 141, Washington, 1975, 216 pp.
34. Anon. *First petrochemical vanadium plant now operating in Canada*, World Petroleum, March 1967, 46-50.
35. Whigham W. *New in extraction: vanadium from petroleum*, Chemical Engineering, March 1, 1965, 64-66.
36. Sirianni G.V and Viens G.E. *Pyrometallurgical recovery of nickel and vanadium from Athabaskan tar sands fly ash*, Department of Energy, Mines and Resources, Mines Branch Investigation report IR 72-23, Ottawa, Canada, June 7, 1972.
37. Stemerowicz A., Bruce R.W., Sirianni G.V and Viens G.E. *Recovery of vanadium and nickel from Athabaskan tar sands fly ash*, Canadian Institute of Mining and Metallurgy Bulletin, **69**, April, 1976, 102-108.
38. Schneider L.G. and George Z.M. *Recovery of vanadium and nickel from oil sand coke ash*, Proceedings Extraction Metallurgy '81, Institution of Mining and Metallurgy, 1981, 441pp.
39. Gomez-Bueno C.O, Spink D.R. and Rempel G.L. *Extraction of vanadium from Athabasca tar sand fly ash*, Metallurgical Transactions B, **12B**, June, 1981, 341-352.

40. O'Neal A.J. *Vanadium recovery from the combustion of Venezuelan fuel oil*, Combustion, **46** (5), 1974, 18-21.
41. Jack T.R, Sullivan E.A. and Zajic E. *Leaching of vanadium and other metals from Athabasca oil sands coke and coke ash*, Fuel, **58**, August, 1979, 589-594.
42. Griffin P.J. and Etsell T.H., Canadian Institute of Mining and Metallurgy Bulletin, **71**, 1978, 137.
43. Griffin P.J. and Etsell T.H, *Extraction of vanadium from oil sand fly ash*, from *Waste treatment and Utilization, theory and practice of waste management*, Volume 2, Moo-Young M. and Farquhar G.J. (Eds.), Pergamon Press, Oxford, 1981.
44. Hanafi Z. and Eid A.E. *Leaching of vanadium from boiler fly ash in alkaline media*, Indian Journal of Technology, **12**, November, 1974, 507-508.
45. Burriesci N., Corigliano F., Primerano P., Zipelli C. and Petrera M. *Influence of iron on the extraction of vanadium from oil ashes*, Journal of the Chemical Society, Faraday Transactions 1, **80**, 1984, 1777-1785.
46. Spink D.R., Rempel G.L. and Gomez-Bueno C.O, *Extraction of vanadium from Athabasca tar sands fly ash*, from *Extraction Metallurgy of refractory metals*, Sohn H.Y., Carlson O.N. and Smith J.T (Eds.), Proceedings 110th AIME Annual meeting, Chicago, 1981, 475 pp.
47. Kostrikin Y.M, Shcherbinina S.P. and Petrova S.Y. *Removing vanadium from the wash water of regenerative air preheaters*, Combustion, November, 1974, 21-22.

48. Szolnoki J. *Utilization of metal bearing industrial waste materials by microbiological leaching*, Proceedings Bacterial leaching '77, Schwartz W. (Ed.), Gesellschaft für Biotechnologische Forschung mbH, 1977, 272 pp.
49. Vojkovic M. *Beneficiation of vanadium-containing materials*, US Patent 3,753,681, 21 August 1973.
50. Vojkovic M. *Improvements in and relating to the beneficiation of vanadium-containing materials*, GB Patent 1,331,932, 26 September 1973.
51. Hahn R., Hess H. and Sattelberger S. *Process for treatment of nickel- and vanadium-bearing residues*, GB Patent 2,153,389, 21 August 1985.
52. Tolley W.K., Laughlin W.C. and Rostoker W. *Recovery of metal values from a metal bearing source of nickel and vanadium*, US Patent 4,276,083, 30 June 1981.
53. Friedman R.H. *Process for recovering metals from waste*, US Patent 4,579,721, 1 April 1986.
54. Guillaud, US Patent 3,873,669, March 1975.
55. Morgan et al, US Patent 4,061,712, December 1977.
56. Goddard J.B. *Alkaline leaching of vanadium bearing residues*, US Patent 4,640,823, 3 February 1987.
57. Hardwick B.A. and Patterson J.H., US Patent 3,826,809, 30 July 1974.
58. Hardwick B.A. and Patterson J.H., US Patent 3,840,637, 8 October 1974.

59. Nutter J.F., Haas F.C. and Thompson D.L., US Patent. 3,656,936, 18 April 1972.
60. Nutter J.F., Haas F.C. and Thompson D.L., US Patent 3,709,974, 9 January 1973.
61. Noel H.M. *Recovery of vanadium*, US Patent 2,372,109, 9 April 1941.
62. Dean G.A. and Herringshaw J.F. *The air oxidation of vanadium (IV) in alkaline solution*, *Talanta*, **10**, 1963, 793-799.
63. Jack T.R, Sullivan E.A. and Zajic E. *The release of vanadium from Athabasca oil sands coke by leaching techniques*, Canadian Institute of Mining and Metallurgy Bulletin, **73**, May, 1980, 151-156.
64. Rodriguez D., Private Communication, Caracas, 1984.
65. Zajic E., Jack T.R and Sullivan E.A. *Chemical and microbially assisted leaching of Athabasca oil sands coke*, Proceedings Bacterial leaching '77, Schwartz W. (Ed.), Gesellschaft für Biotechnologische Forschung mbH, 1977, 272pp.
66. Oberle A. and Scofield T.E. *Process for recovering vanadium from petroleum hydrocarbons*, US Patent 722,309, 25 June 1924.
67. Oberle A. and Scofield T.E. *Process for recovering vanadium from petroleum hydrocarbons*, US Patent 1,638,057, 9 August 1927.
68. Vessely K.D. *Recovery of metals from carbonaceous material*, US Patent 3,522,001, 28 July 1970.

69. McCorriston L.L. *Process using carbonate reagent for recovering vanadium from cokes and ashes derived from heavy oils*, US Patent 4,472,360, 18 September 1984.
70. McCorriston L.L. *Process using carbonate reagent for recovering vanadium from cokes and ashes derived from heavy oils*, US Patent 4,536,374, 20 August 1985.
71. McCorriston L.L. *Process using sulphate reagent for recovering vanadium from cokes derived from heavy oils*, US Patent 4,389,378, 21 June 1983.
72. Haas F.C. and Hesse W.K. *Method for recovering vanadium from petroleum coke*, US Patent 4,243,639, 6 January 1981.
73. Jack T.R., Sullivan E.A. and Zajic J.E. *Comparison of the structure and composition of cokes from the thermal cracking of Athabasca Oil Sands bitumen*, Fuel, **58**, August 1979, 585-588.
74. Schemel R., Rodriguez D. and Salazar R. *Method for leaching and recovering vanadium from vanadium bearing by product materials*, US Patent 4,539,186, 3 September 1985.
75. Bird R.J. and Small N.J.H. *The combustion of heavy fuel oil: some observations on carbonaceous droplet residues and on the ash from the gas stream*, Journal of the Institute of Petroleum, **51** (494), February 1965, 71-77.
76. Allen G.C, Hocking W.H., Watson D.G., Wild R.J. and Street P.J. *Surface studies of coke particles from residual fuel oil combustion*, Journal of the Institute of Energy, **57**, March 1984, 260-265.
77. Goddard J.B. *Salt roasting of vanadium ore in the presence of carbon*, US Patent 4,477,416, 16 October 1984.

78. Queneau P.B. *Recovery of V_2O_5 and nickel values from petroleum coke*, US Patent 4,443,415, 17 April 1984.
79. Sit S.P. *Process for concurrent steam generation and metal recovery*, US Patent 4,524,049, 18 June 1985.
80. Fletcher P.E. and Holm M.M. *Hydrogen production by reaction of carbon with steam or steam and oxygen*, US Patent 3,615,299, 26 October 1971.
81. Gray R.J. and Pesek V. *Petroleum-Coke-Fired cogeneration*, Chemical Engineering Progress, **81**, March 1985, 70-77.
82. Calderon J.L. and Hernandez M. (Eds.). *Proceedings III International Seminar Intevep, Usos alternos del coque*, Intevep, Caracas, 1982, 131 pp.
83. Burkin A.R. (Ed.). *Production of Alumina and Aluminium*, Critical Reports in Applied Chemistry vol 20, John Wiley and Sons, Chichester, 1987, 256 pp.
84. Houston G.J. *A survey of anode consumption in Hall-Heroult cells*, Institute of Inorganic Chemistry, Norwegian Institute of Technology, May 1983, 15 pp.
85. Wright J.K. *The segregation process*, Mineral Science and Engineering, **5** (2), April 1973, 119-134.
86. Iwasaki I. *A thermodynamic interpretation of the segregation process for copper and nickel ores*, Mineral Science and Engineering, **4** (2) 1972, 14-23.
87. Maulden J.C. and Taplin B., *Improvements in or relating to heat treatment of copper ores*, GB Patent 250,991, 1924. *Improvements in or relating to heat treatment and concentration of copper ores*, GB Patent 255,961, 1925. *Improvements in or relating to heat-treatment of oxidized copper ores*, GB Patent 318314, 1927.

88. Annual Report of Mineral Separation Ltd., Mineral Magazine London, **46**, 1932, 200.
89. Rey M.R.W. *Early development of the copper segregation process*, Transactions of Institution of Mining and Metallurgy, **76C**, 1967, 101-107.
90. Freeman G.A., Rampacek C. and Evans L.G. *Copper segregation at the Lake Shore mine*, Journal of Metals, **13**, 1961, 370-372.
91. Pollandt F. and Pease M.E. *Extraction of copper and silver by the segregation process in Peru*, Transactions Institution of Mining and Metallurgy, **69**, 1960, 687-697.
92. Pinkney E.T. and Plint N., *Treatment of refractory copper ores by the segregation process*, Transactions Institution of Mining and Metallurgy, **76C**, 1967, 114-132.
93. Ericson A.S, Svensson J. and Ishii K. *Development of the MINPRO-PAMCO nickel segregation process*, Journal of Metals, **36** (9), September 1984, 42-46.
94. Ericson A.S and Svensson J. *MINPRO mechanical kiln- a new and efficient tool for the nickel segregation process*, Proceedings Extraction Metallurgy '85, Institution of Mining and Metallurgy, London, 1985, 1124 pp.
95. Kagano K, Kojima K. and Takahashi Y. *Extraction of nickel from low grade nickel ores by segregation process*, Proceedings. 9th International Mineral Processing Congress, Prague, **1**, 1970, 319-327.
96. Ser F. and Stojsic A. *Recovery of nickel from laterite ores by a combined method of segregation and flotation*, Proceedings. 8th International. Mineral Processing Congress, Leningrad, **1**, paper D-23, 632-641.

97. Rey M. *Le procede de segregation des minerals de cuivre oxydes pauvres*, Revue Metall., Paris, Memoires, **33**, 1936, 295-302.
98. Rampacek C., McKinney W.A. and Waddleton P.T. *Treating oxides and mixed oxide-sulphide copper ores by the segregation process*, US Bureau of Mines, R.I. 5501, Washington, 1959.
99. Haft N.W. and Sole M.J. *High temperature hydrolysis of sodium chloride in the presence of silica*, Transactions. Institution of Mining and Metallurgy, **81C** (787), 1972, 97-103.
100. Kellogg H.H. *Thermodynamic relationships in chlorine metallurgy*, Journal of Metals, **188**, June 1950, 862-872.
101. Turkdogan E.T. *Physical chemistry of high temperature technology*, Academic Press, New York, 1980.
102. Brittan M.I. and Lidenberg R.R. *Op. Cit. [85]*; Wright J.K. *The segregation process*, Mineral Science and Engineering, **5** (2), April 1973, 119-134.
103. Marples T.N.R. *Kinetic aspects of the treatment of copper ores by the segregation process*, PhD thesis, Imperial College, University of London, 1973.
104. Hadjiat H. *Reactions in the segregation of copper from ores*, PhD thesis, Imperial College, University of London, 1969.
105. Gross P. and Stuart M.C. *On the equilibrium pressure of cuprous chloride in the segregation reaction*, Proceedings Metallurgical Chemistry Symposium, Kubaschewski O. (Ed), HMSO, 1972, 499-411.
106. Mimura H. et al. *Op. Cit. [86]*; Iwasaki I. *A thermodynamic interpretation of the segregation process for copper and nickel ores*, Mineral Science and Engineering, **4** (2) 1972, 14-23.

107. Hardy J.O. *Process for treating vanadium ores*, US Patent 831,280, 18 September 1906.
108. Goddard J.B. and Fox J.S. *Salt roasting of vanadium ores*, from *Extraction Metallurgy of refractory metals*, Sohn H.Y., Carlson O.N. and Smith J.T (Eds.), Proceedings 110th AIME Annual meeting, Chicago, 1981, 475 pp.
109. Gupta C.K. *Extractive metallurgy of niobium, tantalum and vanadium*, International Metal Reviews, **29** (6), 1984, 405-445.
110. Mishra H.C. and Symons M.C.R., *Structure and reactivity of transition metals. Part XIV. Closed-shell in sulphuric acid and oleum*. Journal Chemical Society, 1962, 4411-4417.
111. Gillespie R.J., Kapoor R. and Robinson E.A. *The sulphuric acid system. Part VIII. Solutions of some phosphorus(V) and vanadium(V) compounds*, Canadian Journal of Chemistry, **44**, 1966, 1203-1210.
112. Bond F.C. *Crushing and grinding calculations*, British Chemical Engineering, **6**(6), 378 and (8), 543, 1961.
113. Littler J.S and Waters W.A. *Oxidation of organic compounds with quinquevalent vanadium. Part III. The oxidation of cyclohexanol*, Journal of American Chemical Society, **81**, 1959, 4046-4052.
114. Puutio M. and Vitanen P.O.I. *Vanadium (V). Part VII. Kinetics of the oxidation of triethalammonium ion with vanadium (V)*, Acta Chemica Scandinavica, **A36**, 1982, 689-693.

115. Mehrotra R.N. *Kinetic acidity dependence in certain oxidation reactions. Part II. Oxidation of propane-1,3- and butane-1,4-Diols by quinquevalent vanadium ion*, Journal Chemical Society, B, 1968, 1123-1127.
116. Post K. and Robins R.G. *Thermodynamic diagrams for the vanadium-water system at 298.15K*, Electrochemical Acta, **21**, 1976, 401-405.
117. Clark R.J.H. *The chemistry of titanium and vanadium. An introduction to the chemistry of the early transition elements*, Elsevier Publishing Company, London, 1968, 327 pp.
118. Lindstrom R.E. and Wirth H.E. *Estimation of the bisulphate ion dissociation in solutions of sulphuric acid and sodium bisulphate*, Journal Physical Chemistry, **73**(1), 1969, 218-223.
119. Watts S.F. *The acid leaching of uranium dioxide with peroxygens*, PhD Thesis, Imperial College, University of London, 1985.
120. Young T.F. Rec. Chem. Progr., **12**, 1951, 81. Figure taken from Robinson R.A. and Stokes R.H. *Electrolyte solutions*, chapter 13, 2nd Edition (revised), Butterworths Publications Ltd, London, 1959, 571pp.
121. Cotton F.A. and Wilkinson G., *Advanced inorganic chemistry. A comprehensive text*, 4th edition, John Wiley & Sons, New York, 1980, 1396 pp.
122. Box G.E.P, Hunter G. and Hunter J.S. *Statistics for Experimenters. An introduction to design, data analysis, and model building*, John Wiley and Sons, New York, 1978, 653 pp.
123. Sato N., and Belton G. *The thermodynamics of chlorination of vanadium pentoxide*, Transactions Japan Institute of Metals, **21**(9), 1980, 597-600.

124. Greenwood N.N. and Earnshaw A. *The Chemistry of the Elements*, Pergamon Press, Oxford, 1984, 1542pp.
125. Davies O.L. (ed.) *The design and analysis of industrial experiments*. Second edition, Longman Group Ltd., New York, 1978, 636 pp.
126. Daniel C. *Applications of statistics to industrial experimentation*, John Wiley and Sons, New York, 1976, 294 pp.
127. Kubashenski O., Evans E. LL. and Alcock C.B. *Metallurgical Thermochemistry*, Fourth edition, Pergamon Press, Oxford, 1967, 447 pp.
128. Wagman D.D., Evans W.H., Parker V.B., Halow I., Bailey S.M., Schumm R.H. and Churney K.L. *Selected values of chemical thermodynamic properties. Table for elements 54 through 61 in the standard order of arrangement*, NBS technical note 270-5, US Government Printing office, 1971, 37pp.
129. Kunii D. and Levenspiel O. *Fluidization Engineering*, John Wiley and Sons, New York, 1969, 534pp.
130. Davidson J.F. and Harrison D. *Fluidization*, Academic Press, London, 1971, 847 pp.
131. Vilas Boas L.F. and Costa Pessoa J. *Vanadium*, Chapter 33, from *Comprehensive Coordination Chemistry. The synthesis, reaction, properties and applications of coordination compounds*, Volume 3, Wilkinson G. (Ed.), Pergamon Press, 1987, 1601 pp.
132. Ducret L.P. *Ann. Chim. (Paris)*, 6, 1951, S12, 705.
133. Strehlow H. and Wedt H. *The formation of the vanadyl sulphate complex in aqueous solution*, *Inorganic Chemistry*, 2, 1963, 6-10.

134 Madic C., Begun G.M., Hahn R.L. Lannay J.P. and Thiessen W.E. *Dimerization of aquavanadium (V) ion in concentrated perchloric and sulphuric acid*, Inorganic Chemistry, **23**, 1984, 469-476.

135. Wilkinson G. Private communication, London, January 1988.

136. Dutta S. and Wen C.Y. *Reactivity of coal and char. 2. In oxygen-nitrogen atmospheres*, Industrial and Engineering Chemistry, Process Design Development, **16**, 1977, 31-40.

137. Dutta S. and Wen C.Y. *Reactivity of coal and char. 1. In carbon dioxide atmospheres*, Industrial and Engineering Chemistry, Process Design Development, **16**, 1977, 20-30.

138. Dias M.J.P., PhD thesis, University of London, 1979; Agatzini S., PhD thesis, University of London, 1981; Teixeira L.A.C., PhD thesis, University of London, 1982, Watts S.F., PhD thesis, University of London, 1985; Brandt D.I., PhD thesis, University of London, 1986.

139. Coolidge T.J. *The aqueous pressure of some hydrated crystals. Oxalic acid, strontium chloride and sodium sulphate*. Journal of the American Chemical Society, **42**, 1920, 419-426.

140. Weast R.C. (Ed.), *Handbook of chemistry and physics*, 66th edition, CRC Press Inc., Boca Raton, Florida, 1986.

141. Perry R.H and Chilton C.H. (Eds.), *Chemical Engineers' Handbook*, 5th edition, McGraw-Hill Kogakusha Ltd., Tokyo, 1973.

SUGGESTIONS FOR FUTURE WORK.

The following topics are suggested:

- a) A study by mass spectrometry of the metal chlorides; this would not only unambiguously reveal the metal chloride species present in the gas stream but would provide valuable thermodynamic information, particularly entropies, of the vapour chlorides and oxychlorides of vanadium. Work with pure chlorides and oxychloride and the coke-HCl system would be required. Any polymerization and mixed-metal chloride formation would be revealed by this study.
- b) Further experimentation with the vapour transport experiments. The proposed process would be autogenous and the effect of oxygen on the metal extraction needs to be investigated. Other studies should include an investigation into the unusual effect of flow rate on nickel (the extraction of nickel may be catalysed by another component and mass spectrometry work may reveal possible catalysts) and a full investigation into the removal of iron and sulphur from the cokes.
- c) Investigation into the vanadium, nickel, iron and sulphur extraction behaviour in the vapour transport reaction using Delayed coke.
- d) An investigation into the suitability of the reacted cokes for anode production. This should include the making of anodes, measurements of their chemical and physical properties and aluminium electrolysis test (to find current efficiencies and possible aluminium contamination).
- e) An economic evaluation of the vapour transport process.
- f) Further studies into the complexation chemistry of vanadium (V) and vanadium (IV) in sulphuric acid solutions.

ACKNOWLEDGEMENTS.

I like to express my sincere thanks to my supervisor, Dr A.J. Monhemius, for his advise, encouragement, help and friendship; and to Prof. A.R. Burkin for his many encouraging comments and useful discussions.

I also like to express my gratitude to the present and past members of the Hydrometallurgy group for their friendship, camaraderie, advise, criticism and for helping to make all such good fun. Good luck to you all!

My thanks are due to the Institution of Mining and Metallurgy and the Committee of Vice-Chancellors and Principals of UK Universities for their financial support in the form of the Stanley Elmore Fellowship and the Overseas Research Scholarship.

Many thanks to Mrs E. Lewis for the Electron microscopy work; Mr D. Shillam and Mrs J. Heeley for the XRF analysis; and Mr M.J.L. Haddon, Mr J.W. Wright and Mr. J.E.A. Burgess for their general help and assistance.

Thanks are also due to Intevep S.A. for supplying the cokes.