THE RECOVERY OF PURIFIED COAL FROM SOLUTION

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SYNOPSIS

The recovery of purified coal from solution

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A new process is being developed to produce graphite from prime coking coal. Coal is dissolved in dimethylformamide (DMF), on addition of sodium hydroxide. The minerals and undissolved coal are separated by centrifugation and filtration to give a solution (referred to as Refcoal solution or RCS). Over 90 wt % of the organic part of a flotation product, from the Tshikondeni mine, can be dissolved at temperatures ranging from room temperature to 135°C. The purified coal (referred to as Refcoal) and DMF need to be separated – the Refcoal to be coked and the DMF to be purified and recycled. This process should be as efficient as possible, whilst both products should be low in water content to minimise drying costs.

The addition of water to the Refcoal solution causes precipitation to take place, forming a gel (referred to as Refcoal gel) liquid system. This mixture can be either centrifuged or filtered to give a denser gel, containing water, DMF and coal solids, and supernatant or filtrate, containing water and DMF.

Different techniques and processes can be used to improve the separation of the DMF from the Refcoal by achieving a denser Refcoal gel:

- Longer centrifugation times improve the density and therefore the separation, but this technique has its limits.
- The use of low-temperature water improves the separation.
- The use of syneresis could improve separation at a lower cost: heated standing tanks are used to expel the supernatant and therefore increase the density of the gel, thereby decreasing the required number of washing stages.

- The addition of toluene at the beginning of a wash improved the removal of DMF by 20%, using centrifugation as separation method.
- Pressure filtration gave a 20% improvement on centrifugation, with no additives.
- The addition of toluene to the pressure filtration process gave another improvement of 15%, and after three stages the percentage of solids in the gel was 28% – the highest so far achieved. This method also resulted in the highest removal of DMF in the first stage (73% of the original DMF in the RCS was removed).

Counter-current washing shows the greatest potential, using the least amount of water. The concentration of DMF in the wash solution, to gel the Refcoal solution, is a limitation of this process. If the concentration is too high, no gelling and therefore no separation can take place in the first stage. It is recommended that counter-current washing using pressure filtration should be investigated; however, this will be difficult on a laboratory scale due to the mass losses during transfers.

Keywords: coal extraction, purified coal, dimethylformamide, precipitation, coal gel, agglomeration, toluene, pressure filtration, centrifugation, separation

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ABBREVIATIONS AND SYMBOLS

Abbreviation	**Description**
CVD	Chemical vapour deposition
d.a.f.	Dry ash free
d.m.f.	Dry mineral free
DMAC	Dimethylacetamide
DMF	Dimethylformamide
HCl	Hydrochloric acid
HTR	High-temperature reactor
LWG	Lengthwise graphitisation
m.a.f.	Mineral and ash free
NaOH	Sodium hydroxide
NMP	N-methyl-2-pyrrolidinone
PBMR	Pebble Bed Modular Reactor
ppm	Parts per million
RCF	Relative centrifugal force (in g forces)
RCG	Refcoal gel
RCS	Refcoal solution
Refcoal	Purified coal
r/min	Revolutions per minute
THN	Tetra-hydro-naphthalene
wt %	% based on mass
Symbols	**Description**
$C_{DMF}\%$	Mass % of DMF left in RCG after wash stage on the basis of total DMF in RCS
$C_{DMF,RCG,x}$	Concentration of DMF left in RCG_x (g/g)
$M_{DMF,RCG}$	Mass of DMF in RCG (g)
$M_{DMF,RCS}$	Mass of DMF in RCS (g)
n	Mass fraction of DMF in supernatant after first wash
RCG_x	RCG exiting stage x (g)
RCS_0	RCS entering stage 1 (g)

Symbols	**Description**
S_x	Supernatant exiting stage x (g)
S_x'	Real supernatant exiting stage x (g)
x	Number of stages (washing)

Chapter 1. INTRODUCTION

Graphite is used worldwide in various applications. One important application is in nuclear reactors; such a reactor is being developed by Eskom, PBMR (Pty) Ltd. The construction of the reflector of this reactor requires around 600 tons of nuclear-grade graphite. The use of coal instead of petroleum products is preferred due to the limited availability of petroleum products and because coal is readily available in South Africa. In collaboration with the University of Pretoria, a new process is being developed to produce graphite from high-rank coals (Morgan, 2002).

This new process uses “Refcoal”; which is a process where solution purification is used to dissolve the organic part of suitable coals in a polar aprotic solvent, thereby separating the organic and inorganic parts of the coal (Morgan, 2002). Dimethylformamide (DMF) is used as organic solvent for the extraction of the coal.

This study entails the development of a process for the recovery of the solvent, for recycling, with the Refcoal as the product. Previous experiments have shown that a gel forms with the addition of water to the Refcoal solution (Resenga, 2001; Kitching, 2002; Manganyi, 2001; Morifi, 2002). When this gel is centrifuged, a supernatant top layer and a denser gel bottom layer form. The DMF dissolves into the water and is therefore removed by it via the supernatant. This study investigates the factors that affect the washing efficiency, such as the wash water quantity and temperature, the stirring and centrifuging times, the effect of pH on the separation and the effects of agglomeration oils. Different separation techniques are also investigated, such as direct evaporation, centrifuging and filtration.

It is important that the residual water in the Refcoal and in the DMF is minimal. Evaporating water from the Refcoal is energy-intensive and to separate the DMF from the water via distillation will be costly due to the close boiling temperatures of DMF and water. Therefore it is important to have a minimal water content in the Refcoal before evaporation and in the DMF before distillation.

Chapter 2. BACKGROUND

2.1. Pebble Bed Modular Reactor

Eskom South Africa, in co-operation with other companies, is developing the Pebble Bed Modular Reactor (PBMR), which will be a small, safe, clean, cost-efficient, inexpensive and adaptable nuclear power plant.

The PBMR nuclear power plant uses coated uranium particles encased in graphite to form a fuel sphere. In addition, the PBMR design makes use of helium as the coolant and energy-transfer medium to a closed-cycle gas turbine and generator.

This design differs in a number of ways from Pressurised Water Reactors. These design differences result in the PBMR being an inherently safe and economical power plant (PBMR, 2003).

The PBMR depends on various forms of carbon materials for its construction and operation. The reflector, which acts as an immediate container for fuel pebbles, is constructed from 600 tons of nuclear-grade graphite. The fuel spheres are mostly carbon, containing only 9 g of uranium oxide in a ball made of 200 g of graphite (Morgan, 2002).

Due to the large quantity of graphite needed for the PBMR, alternative methods of manufacturing this nuclear-grade graphite need to be investigated. The use of petroleum products would not be sufficient due to the limited availability of petroleum products; coal is therefore preferred because it is readily available in South Africa (Morgan, 2002). This is where the Refcoal process will be used. The ash content of high-rank coals is removed using an alkali-enhanced extraction process with an organic solution as solvent.

The following sections give some more information on the PBMR.

2.1.1. Reactor

The PBMR is a helium-cooled, graphite-moderated High-Temperature Reactor (HTR). It consists of a vertical steel pressure vessel, approximately 6 m in diameter and 20 m high. The pressure vessel is lined with a layer of graphite bricks, made from synthetic graphite. Depending on the position within the structure, the blocks are of different qualities. The inner graphite layers, serving as the top, bottom and side reflectors, are used to reflect the neutrons generated by the nuclear reaction and a passive heat-transfer medium. They should be able to withstand high temperatures (up to 950°C). The control-rod channels and the boron absorber ball channels are located in the side reflector. Carbon bricks, containing boron, surround the graphite reflectors; they act as a neutron shield to prevent the activation of the steel shell. The specifications for each of the forms of carbon employed in the PBMR are exacting, with regard to both chemical purity and physical structure and form. The reflector graphite must be, on the atomic scale, highly anisotropic, yet, on the reactor scale, it must be very isotropic in its properties (Morgan, 2002; PBMR 2003; Jing *et al.*, 2002; Marsden, 2000).

2.1.2. Fuel pebbles

When fully loaded, the core will contain approximately 456 000 fuel spheres. The fuel elements of the PBMR are graphite spheres, 60 mm in diameter, containing many uranium oxide (UO_2) beads (9 g), coated to contain the fission products. The uranium used has an enrichment of 8% (Nicholls, 2002). Isotropic pyrolytic carbon exhibits excellent stability under neutron irradiation. This, coupled with its high strength, dense isotropic structure and impermeability to gases, makes it the material of choice for the coating of nuclear fission particles to contain the fission products. The coating is produced in a fluidised bed via chemical vapour deposition (CVD) (Pierson, 1993: 162). The layers consist of (from the inside out) (see Figure 2.1.1):

- Porous carbon layer (90 µm)
- Inner dense pyrolytic carbon layer (40 µm)
- Silicon carbide layer (35 µm)
- Outer dense pyrolytic carbon layer (40 µm).

The final particle is approximately 1 mm in diameter.

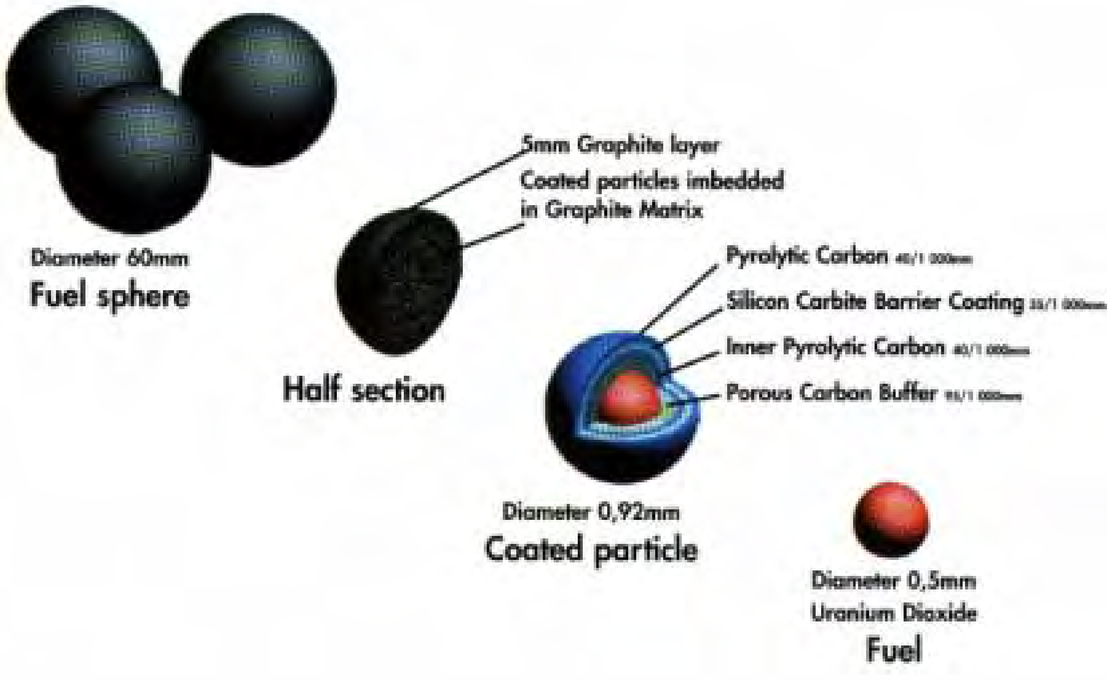


Figure 2.1.1: Fuel element design for PBMR (PBMR, 2003)

The coated particles are mixed with finely powdered natural and synthetic graphite and phenolic binder resin, and moulded into spherical shapes (50mm in diameter). This sphere is pressed into a 5-mm-thick hemispherical shell of pure graphite. After being baked to about 900°C under vacuum, the pebbles are machined to produce near-perfect spheres with diameters of 60 mm, and are ready for use. The product is a smooth and tough spherical ball, as shown in Figure 2.1.2.

Figure 2.1.2: Fuel spheres for PBMR (PBMR 2003)

The ceramic-coated particles are a very durable final residual waste form that will remain impervious to moisture well beyond the life of the metal containers currently being considered for spent fuel disposal (Rodriguez *et al.*, 2003).

2.2. Synthetic Graphite

As described above, the PBMR requires significant quantities of graphite, especially nuclear graphite, for its construction. Synthetic graphite is used not only in nuclear systems, but also in a large variety of other applications. For example (Pierson, 1993: 110-120, 161-163, 267-278; Delhaès, 2001: 183-193; Inagaki, 2000: 65-68):

- Moulded graphites are used for electrodes, boats and dies, as structural components for fuel cells, as lubrication and in chemical reactors.
- They are used for carbon and graphite fibres.
- Pyrolytic graphite and carbon are used in biomedical applications, such as heart valves and dental implants. They are also used as coatings for moulded graphites to provide a smooth and pore-free surface, and to coat fibres. In addition, they are used in the manufacture of re-entry heat shields, rocket nozzles, aircraft disk brakes, and other aerospace components.
- Lastly, they are used in graphite foams (Hayward, 1997; Difilippo, 2004).

2.2.1. Background on non-graphitisable and graphitisable carbons

To manufacture synthetic graphite, one must understand the difference between graphitisable and non-graphitisable carbons.

Isotropic (i.e. non-graphitisable) carbons originate from materials that are already macromolecular in nature, e.g. the cellulose or lignin components of wood; synthetic resin as used in the chemical industry; and specific cross-linked structures of low-rank coals. These isotropic carbons maintain their polymeric character on pyrolysis, without fusing, the carbon being a pseudomorph of the parent substance.

Anisotropic (i.e. graphitisable) carbons are generated from pitches and coals. These materials fuse on pyrolysis and it is from within this liquid phase that polynuclear, aromatic, discotic, nematic liquid crystals (mesophase) are generated by the process of homogeneous nucleation. Mesophase is the precursor to anisotropic structure in carbons/cokes; it is known as a liquid crystal phase. Coal carbonisation is more complex than pitch pyrolysis because of the need to depolymerise the original coal structure before liquid crystals can be generated from within the fluid coal.

Structure in both isotropic and anisotropic carbons is based on the sp^2 carbon nano-structure, although in very defective forms. Isotropic carbons have lamellae arranged randomly with associations of small number to give an indication of short range order. Anisotropic carbons have essentially approximately parallel arrangements of lamellae, which subsequently assume increased order on the heat treatment of a given graphitic material (Marsh, 1989: 1, 37, 39).

2.2.2. Properties of synthetic graphite

All graphite materials that have some application in industry are polycrystalline. Most of them consist of grains, which are also composed of units of parallel-stacking carbon hexagonal layers similar to graphite, called crystallites. The properties of polycrystalline graphite materials therefore, depend strongly on the statistical distribution of grains and also on that of the crystallites inside the grains. The crystallites are highly anisotropic, as in graphite single crystals, and as a consequence the grains are also more or less anisotropic.

Polycrystalline graphite materials have the following fundamental characteristics:

1. High thermal resistance in a non-oxidising atmosphere
2. High chemical stability
3. Non-toxic
4. High electrical and thermal conductivities
5. Small thermal expansion coefficient and, as a consequence, high thermal-shock resistance
6. Very lightweight, with a bulk density of 1.5 to 2.2 g/cm^3
7. High mechanical strength at high temperatures
8. High lubricity
9. Biocompatible
10. Radiation-resistant
11. Low absorption cross-section and high moderating efficiency for neutrons.

The bulk properties of polycrystalline graphite materials are strongly governed by the preferred orientation of the crystallites, due to the alignment of the grains and also the textures inside the grains, and, moreover, due to the thermal history that they have experienced, primarily the maximum treatment temperature. The alignment of the grains depends on the precursor and the conditions of their forming process. The texture decides the size and structural perfection of the crystallites. The manufacturing process is therefore very important – it will influence the properties of the synthetic graphite just as much as the graphitisability of the carbon used.

Details of the production of isotropic high-density graphite have not been published due to their extreme confidentiality. For this reason, old data are referred to in order to understand the importance of some of the production parameters (Delhaès, 2001: 179-180).

2.2.3. Manufacturing of synthetic graphite

2.2.3.1. Raw materials

The selection of the appropriate raw materials (precursor) is the first and most critical step in the process of manufacturing synthetic graphite. It determines both the properties and the cost of the final product. The characteristics of these raw materials, such as the particle size, the ash content of the cokes and the degree of carbonisation of the pitch, must be taken into account.

Raw materials can be divided into four generic categories: fillers, binders, impregnates and additives (Pierson, 1993: 88-89).

Fillers form the base of the graphite material; they are normally a type of coke, but can also be recycled or natural graphite. The filler is usually selected from carbon materials that graphitise readily (Marsh & Reinoso, 2000: 174-176, 195-285). Such materials are generally cokes that graphitise rapidly above 2 700°C. Other major fillers are synthetic graphite from recycled electrodes, natural graphite and carbon black (Pierson, 1993: 89). The main cokes used in industry are petroleum coke and coal-tar pitch coke. Coal-tar pitch coke is a desirable raw material, but in most countries the supply is not sufficiently secure to form the basis of a carbon industry (Marsh & Reinoso, 2000: 174-176, 195-285). Petroleum coke is the filler of choice in most synthetic graphite applications (Blackman, 1970: 51; Ubbelohde & Lewis, 1960: 21).

The binder used is either a pitch or in some cases a resin (Marsh & Reinoso, 2000: 174-176, 195-285). The function of the binder is to plasticise the coke powder so that it can be formed into bodies of the required shape or size, which have enough rigidity for handling in the later stages of the process (Blackman, 1970: 53). Another role of the binder is to give electrical contact. Binder requirements are concerned mainly with good wettability and penetrability of the binder to the coke particles (Marsh & Reinoso, 2000: 174-176, 195-285). Subsequently, the material must carbonise with a good yield in order to provide a strong, dense body. The preferred binder material is coal-tar pitch, which softens at temperatures around 80°C and hardens again on cooling (Blackman, 1970:53).

Other binders, such as petroleum pitch and thermosetting resin, are used for speciality applications (Pierson, 1993: 90). As with coal-tar pitch, the chemical and physical characteristics are very dependent on the manufacturing process and the conditions used, especially the process temperature and heat-treatment time (Marsh, 1989:80).

Binder pitches are also used to impregnate the carbonised material to improve its density, and additives such as iron and iron compounds are added to inhibit puffing during graphitisation (Marsh & Reinoso, 2000: 174-176, 195-285).

2.2.3.2. Milling and sizing

Calcined coke filler and binder are ground or milled to the particle size requirement to remove the gross porosity (Blackman, 1970: 52; Pierson, 1993: 91; Ubbelohde & Lewis, 1960: 21). A batch usually consists of more than one size. This allows better control of packing characteristics and optimises the density of the final product.

For nuclear graphite, the main criteria are the production of highly pure carbon, to prevent the absorption of low energy neutrons, and no preferred orientation of the graphite crystallites, to confer high dimensional stability. The optical texture of the coke is mostly fine grain, with random orientation (Marsh & Reinoso, 2000: 199).

2.2.3.3. Mixing and forming

Filler and binder are weighed in the proper proportions. This mixture is blended with large mixers into a homogeneous mix in which each filler particle is coated with the binder. Blending is usually carried out at 160–170 °C (Ubbelohde & Lewis, 1960: 22), although temperatures may reach as high as 315°C. When mixing at lower temperatures (below the melting point of the binder), volatile solvents such as acetone or alcohol are often added to promote the binder dispersion (Pierson, 1993: 91).

Three major forming techniques are used to form the graphite mix: extrusion, compression (uniaxial loading) and isostatic pressing. They are shown in Figure 2.2.1 (Delhaès, 2001: 183). The selection of a particular technique has a great influence on the final properties of the moulded product, as shown in Table 2.2.1 (Pierson, 1993: 91-92).

Table 2.2.1: Characteristics of forming techniques (Pierson, 1993: 93)

Technique	**Characteristics**
Extrusion	Anisotropic properties Non-uniformity of cross-section Presence of flow lines and laminations Low cost
Compression	Non-uniformity Edge effect Presence of flow lines and laminations Medium cost
Isostatic	Isotropic properties Uniformity No flow lines and laminations High cost

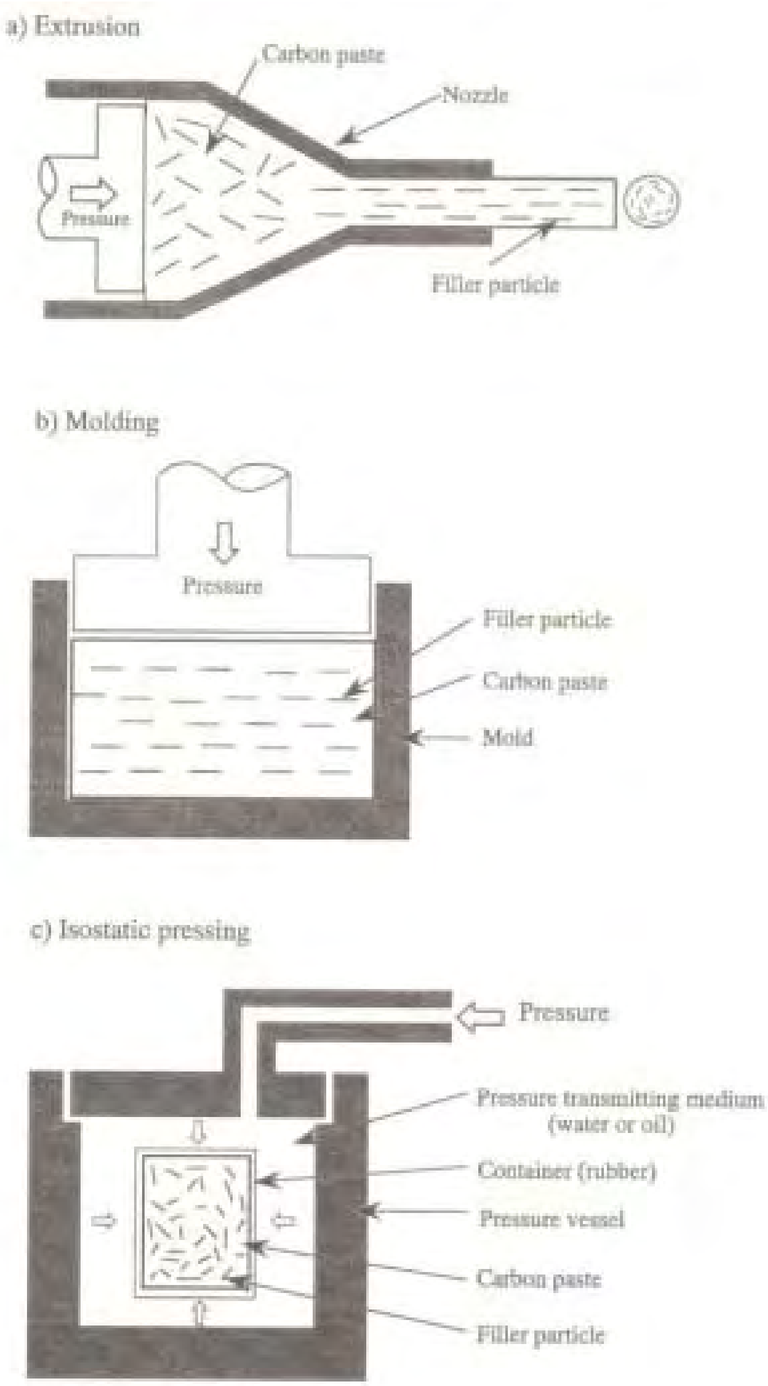


Figure 2.2.1: Scheme for the forming processes of carbon pastes. In order to illustrate their preferred orientation, flaky filler particles are shown (Delhaès, 2001, 184)

2.2.3.4. Baking

The cooled moulded or extruded "green" blocks are fired after cooling, during which the binder is pyrolysed (Blackman, 1970:54). This takes place under an inert or reducing atmosphere (Pierson, 1993: 95). This firing process must be carried out extremely carefully because loss of the volatile matter, combined with shrinkage of the binder, takes place. It is conventional to raise the temperature to about 600°C at slow heating rates, which may vary between 2°C/h and 10°C/h during the firing cycle (Blackman, 1970: 55). The bonded mixture evolves hydrocarbons in the region of 300 to 500°C and becomes rigid at 450°C (Ubbelohde & Lewis, 1960: 22).

The temperature is then raised to between 760 and 980°C. This can be done faster than the first temperature step since most of the volatiles have been removed, the material is already rigid and sagging is no longer a problem (Pierson, 1993: 95). With large bulk-packed furnaces, the firing cycle may last about six weeks (Ubbelohde & Lewis, 1960: 22).

The application of pneumatic pressure (±12.4atm), during baking, resulted in higher carbon densities of ±1.70 g/cm^3, whereas non-pressurised baking gave densities of about 1.60 g/cm^3 (Blackman, 1970: 56).

In order to improve the porosity and increase the density, an impregnation stage is frequently inserted before the final graphitisation. A subsequent carbonisation step converts the impregnant to useful carbon, giving a density increase of about 0.15 g/cm^3 and an improvement in other properties, such as electrical conductivity (Blackman, 1970: 56).

2.2.3.5. Graphitisation

The product from baking is a solid block, with somewhat less than the “green” body, but otherwise in its physical and chemical properties broadly similar to the carbon powder used as starting material. It normally has a density in the range of 1.5–1.7 g/cm^3, electrical resistivity of the order of 4×10^{-3} Ω cm, and is hard and abrasive (Marsh & Reinoso, 2000: 10-12).

For many applications, for example electrodes in steel melting furnaces, or nuclear reactor construction, it will be subjected to graphitisation. The process involves heating the blocks in the absence of air, to a temperature in the range of 2 500–3 000°C. The temperature is raised over a few days, and is maintained for a few hours. Heating is ceased and the blocks are allowed to cool until their temperature has fallen to the point where the blocks may safely be exposed to air (Blackman, 1970: 56-57).

This temperature cycle is shorter than the carbonisation cycle and varies depending on the size of the part, lasting from a few hours to as long as three weeks. It is usually performed in a resistance furnace (the original Acheson cycle) or in a medium-frequency induction furnace (Pierson, 1993: 95).

Heating of the carbonised rods by direct joule effect (using the so-called Lengthwise Graphitisation Furnace – LWG) has been developed. For the conventional Acheson process, about one month is required to complete the graphitisation treatment. Only about one week is required for the newly developed LWG process. Induction heating of the carbon rods prevents contamination from the packing mixtures (Delhaès, 2001: 183).

2.2.3.6. Purification

The graphitisation step is an effective means of removing metallic impurities since most oxides are reduced under these conditions and the resulting metal is volatilised from the stock to the packing. The loss of impurities on graphitisation is indicated in Table 2.2.2 (Blackman, 1970: 58).

Table 2.2.2: Effects of graphitisation on impurity content (Blackman, 1970: 58)

Element	Impurity Content (ppm)	
	Baked block	Graphitised block
Ash	11 000	500
Sodium	2 900	9
Silicon	490	93
Aluminium	250	8
Iron	225	34
Nickel	125	7
Calcium	110	85
Vanadium	87	52
Lead	40	0.4
Magnesium	40	0.2
Chromium	23	0.6
Boron	0.32	0.18

Vanadium and boron do not respond well to this process, both forming refractory carbides. In addition, boron is capable of substitution within the graphite lattice without distortion. Both these elements are undesirable in graphite for nuclear applications because of their high capture cross-section for thermal neutrons. Boron is specified not to exceed a few tenths of a part per million (ppm). Special means are therefore adopted for the provision of such pure products. One method is to take particular note of the boron contents when selecting the filler coke and binder.

An alternative method, which permits more freedom in the choice of the filler coke, is to purify the graphite by halogen treatment, either separately or during the graphitisation process (Blackman, 1970: 58-59). This treatment can remove impurities such as aluminium, boron, calcium, iron, silicon, vanadium and titanium to less than 0.5 ppm (Pierson, 1993: 96) and reduces the total ash to under 20 ppm (Ubbelohde & Lewis, 1960: 23). The currently more favoured method is to introduce sodium fluoride into the graphitising furnace (Marsh & Reinoso, 2000). Boron and other impurities are then volatilised out as fluorides (Blackman, 1970: 59).

2.3. Nuclear Graphites

Nuclear graphite is used as a moderator in nuclear fission reactors. This moderator slows down the fast neutrons formed during the nuclear fission reaction via collision.

A good moderator should possess the following properties (Ubbelohde & Lewis, 1960: 20; Marsh, 1989: 17; Delhaès, 2001: 93):

- The moderator should not react with the neutrons. If the neutrons are captured in the moderator, they are lost to the fission process. Therefore the moderator has to have a low cross-section for neutron capture.
- Neutrons should be slowed down over a short distance and with few collisions in the moderator.
- The moderator should be inexpensive, yet must satisfy the reactor core's structural requirements, and must be compatible with other construction materials.
- The moderator should not undergo deleterious physical and chemical changes when bombarded with neutrons.
- A good moderator must thermalise fast neutrons efficiently.

The choice of potential moderators is, in practice, limited to a handful of elements of atomic number less than 16. Gases are of limited use as moderators because of their low density. The choice of potential moderators of practical use rapidly reduces to just four materials. Water is relatively unaffected by neutron irradiation, is low cost and easily obtained. However, neutron absorption in the hydrogen is high (Delhaès, 2001: 93-94).

Heavy water (deuterium oxide) is a particularly good moderator because ${}_1H^2$ and ${}_8O^{16}$ do not absorb neutrons. However, the cost of separating the heavy hydrogen isotope is high.

Beryllium and beryllium oxide are good moderators but are toxic and are also expensive and difficult to machine.

Graphite is an acceptable moderator. It offers an acceptable compromise between nuclear properties, cost and utility as a structural material for the reactor core. Unfortunately, the properties of graphite are markedly affected by neutron irradiation due to its porosity (Delhaès, 2001: 93-94).

Nuclear radiation affects the crystal lattice of the graphite, which becomes distorted by collisions with fast neutrons, other energetic particles and displaced carbon atoms. As a result, the properties are altered. Strength and hardness generally increase and dimensional changes become noticeable, particularly at high temperature (Ubbelohde & Lewis, 1960: 20).

Nuclear graphite is usually manufactured from high-grade coke filler and pitch binder, processed as described earlier, and then thoroughly purified by halogen treatment (Pierson, 1993: 120). The highest purity is necessary to prevent the absorption of low-energy neutrons, and no preferred bulk orientation of graphitic crystallites is necessary to give high dimensional stability (Marsh & Reinoso, 2000: 117-120). The resulting optical texture is, therefore, mostly fine grain with random orientation (Marsh, 1989: 17).

Chapter 3. LITERATURE

3.1. Extraction Processes

The direct coking of coals does not give a graphitisable coke due to the high amounts of impurities in the coal. Extraction processes dissolve the organic part of the coal into an organic solution, and so separate the impurities (inorganic materials) out of the coal. The following sections discuss the different processes so far developed.

3.1.1. Alkali-enhanced extraction

3.1.1.1. Summary of the process

'Refcoal' is purified or refined coal. It was originally developed by the CSIR and is now being further developed by the University of Pretoria, which offers a means of pre-purifying coking coals by an alkali-enhanced process. The Refcoal process involves dissolving the organic part of the coal into an organic, polar aprotic solvent by adding a small amount of alkali, which acts as a catalyst. Dimethylformamide (DMF) is highly suitable as an organic solvent, being the least expensive option and technically advantageous from a solvent-recovery perspective. Sodium hydroxide is, in general, both technically and economically the alkali of choice (Morgan, 1995). The process of extracting the organic materials takes place at operating temperatures ranging from room temperature to just below the boiling point of DMF (±153°C).

The extraction process is done under an inert atmosphere of nitrogen. Most studies have been done on a flotation concentrate coal from Kumba's Tshikondeni mine, with 8% ash. For this coal 90-92 wt % (d.[illegible]) of the organic material goes into solution during the extraction process. The Refcoal solution is separated from the inorganic materials via centrifugation. The ash content is reduced from ±10% to 0.2% (Morgan, 1992); this could be improved with a better separation technique (Morgan, 2004). Refcoal is then recovered from this solution by precipitating the coal from the DMF with water and drying off the water via evaporation (Morgan, 2002).

The Refcoal is then coked in a furnace at 500°C for an hour, after which the temperature is raised to 900–1 000°C and kept there for two to three hours. The coking takes place under a nitrogen atmosphere to prevent oxidation. The first stage of heating is important: the temperature is raised at approximately 1°C/min as this is the stage in which time is needed to form the mesophase, which in the end will determine the graphitisability of the coke (Phulpheli, 2004).

This coke can then be used for various applications.

3.1.1.2. Proposed applications

The possibilities for the end-use of Refcoal are determined by the effort (or investment) required for the development of each process to the point where the technical and economical risks are acceptable (Morgan, 1992).

The main application being investigated is nuclear-grade graphite for use in the Pebble Bed Modular Reactor.

Other possible applications include (Morgan, 1992):

- Metal carbides, for example silicon carbide with a fine particle size, could be used for mechanical seals, heat exchangers and burner nozzles.
- Metal carbide/carbon composites show promise as bearings and mechanical seals for use under high temperatures and in oxidative environments.
- The carbon in Refcoal could be used as a reductant for preparing metal nitrites.
- The cost of carbon fibres is too high for bulk consumption. Refcoal-based fibres offer the possibility of a much lower cost which, if realised, together with properties similar to those of glass fibres, could lead to a revolution in the use of carbon-reinforced cement in the building industry and the creation of a very large new market.
- Activated carbons can be manufactured from Refcoal due to its high carbon yield and low impurity content.

- Engineering carbons are used extensively where aggressive conditions need to be met; glassy carbon and fine-grained graphite are two of these carbon forms.
- The market for electrode carbons and binders in South Africa is very large and at present the bulk of high-quality carbons are being imported. Refcoal could give a product of higher quality and capacity.
- Refractory binders – Refcoal solution or paste could be a suitable binder in the metallurgical industry which uses large quantities of refractory bricks made from magnesia and graphite, currently being bound with resin.
- Metallurgical reductant and fuel – Refcoal is a chemically attractive metallurgical reductant due to its low impurity levels (including phosphorous). While the price of crude-oil based fuels remains low, the cost of developing Refcoal for use as a fuel for diesel or gas turbine engines would be too high.

3.1.1.3. Extraction method

The general extraction procedure is done at 95°C, but the temperature could be varied between room temperature and the boiling point of DMF (±153°C). The extraction is done in a jacketed reactor. The ratio of raw materials used, i.e. DMF:Coal:NaOH, is 100:10:1 (by mass). At a temperature of 135°C or higher, a ratio of up to 100:30:3, could be used. The DMF and the coal are added to the reactor and stirred continuously while the reactor temperature rises. The whole extraction is done under a nitrogen atmosphere, at atmospheric pressure. As soon as the mixture reaches the desired temperature, the NaOH is added. When 90-92 wt % of the coal has been absorbed into the DMF, the extraction is stopped. This is determined by measuring the absorbance of a diluted sample. The reactor content is then centrifuged for one hour to separate the Refcoal solution from the inorganic material and undissolved coal. The Refcoal solution contains approximately 8wt % coal. This refined coal recovered from the Refcoal solution contains approximately 2.0 wt % ash. Further process development is required to increase the efficiency of separation of the undissolved material and the Refcoal solution. The use of filtration is an option (Morgan, 2004).

During room-temperature extraction, the temperature is kept constant. This method can take can take anything from 24 hours to 72 hours, depending on the stirring efficiency.

At present the extraction temperatures used do not exceed 135°C due to equipment restrictions. At this temperature, extraction takes about two to three hours. Using higher coal ratios increases the amount of coal in the Refcoal solution to 10–21 wt %. Additional optimisation of this extraction method is still needed (Kalamba, 2004).

3.1.2. Other efficient coal-extraction techniques

The Refcoal process of the University of Pretoria in South Africa is not the only extraction process. Studies have also been done by institutes in the USA and Japan.

3.1.2.1. Extraction using hot N-methylpyrrolidinone as solvent

The Department of Chemical Engineering and Chemistry at the West Virginia University, USA, developed a process for the preparation of ultra-low-ash coal extract under mild conditions (202°C and 1 atm) (Renganathan *et al.*, 1988). This ultra-clean coal can be used for combustion and to avoid the need for costly systems to treat stack gas.

The extractions were carried out in N-methyl-2-pyrrolidone (NMP) under an inert nitrogen atmosphere. Boiling NMP (202°C) was added to the coal in a 10:1 mass ratio. After being stirred for 60 min, the content was filtered at 200°C under vacuum. The unextracted residue was washed with additional NMP at 200°C, cooled to room temperature and then washed with diethyl ether and dried in a vacuum oven. The filtrate was allowed to cool to room temperature and distilled water was added to precipitate the coal extract, after which it was separated using vacuum filtration. The solid extracted was washed with three portions of methanol and dried in a vacuum oven.

The percentage extraction was found to be as high as 74% (m.a.[illegible]nd the ash content was as low as 0.1%. This method compares well with that of the University of Pretoria, although higher temperatures are needed and a lower extraction is achieved. The percentage ash left in the extracted coal is lower, but the University of Pretoria's separation technique could be improved to reach the same results. Also, DMF is a cheaper solvent than NMP (Morgan, 2004).

3.1.2.2. Hypercoal process

The hypercoal process is the production of ashless coal at high yield, mainly for use in power generation. The study was done by the Institute of Energy Utilisation, National Institute of Advanced Industrial Science and Technology; and the College of Science and Technology, in Japan.

The solvent extraction for hypercoal is done at an operating temperature ranging from 200 to 380°C using various organic solvents, and the extraction takes place under nitrogen (Yoshida *et al.*, 2002).

Using a flow-type extractor with a 1 MPa nitrogen atmosphere, 0.5 g of coal was extracted for 60 min with 0.1 ml/min of fresh solvent. Both extraction and filtration were done at 360°C. A large amount of n-hexane was added to the solution to precipitate the extract components, which were then filtered and washed with toluene and n-hexane, and dried. It was possible to obtain extraction yields of more than 60 wt.% (d.m. with ash contents of <0.1 wt %. Coals with a lower softening point also give higher extraction yields. Moreover, using crude methylnaphthalene oil, an extraction yield of ~80% can be achieved (Yoshida *et al.*, 2004).

Masaki *et al.* (2004) found that when the coal used in the extraction was pretreated with acid, the extraction yield increased. Also, when additives such as NMP and quinoline were added, they increased the extraction yield. However, neither the pretreatment nor the additives could increase the extraction yield above 80 %.

This method used higher temperatures than the Refcoal process. It also had a lower extraction yield. The ash content was lower, but as mentioned in Section 3.1.2.1, the Refcoal process can be improved.

3.1.2.3. Extraction using mixed CS_2-N-methyl-2-pyrrolidinone solvent

Extraction at room temperature was done by the Chemical Research Institute of Non-Aqueous Solutions, at Tohoku University in Japan. They used a CS_2

and NMP mixed solvent (1:1 by volume) to extract the coal at room temperature. A coal:solvent mass ratio of 1:25 was used. The coal and solvent were mixed under ultrasonic irradiation for 30 min at room temperature. After centrifugation, the supernatant was separated by decantation. Fresh solvent was added to the residue, which was again extracted for 15 min and centrifuged. These procedures were repeated until the supernatant became almost colourless (~5 to 7 times). The supernatant was filtered and the solids added to the residue (Iino *et al.*, 1988).

Wet extract was washed with acetone three times to remove the NMP. The acetone-soluble fraction of the extract was washed with an acetone-water solution. The extract was dried under vacuum overnight (Iino *et al*, 1988). Extraction yields of up to 63 wt % (d.a.f.) were obtained with an ash content <0.1 wt %. (Iino *et al.*, 1989).

This process uses large amounts of the extraction solvent; therefore it would be more expensive than the Refcoal process. It also has a lower extraction yield. The advantage is that it is done at room temperature and therefore saves energy.

3.2. Recovery of Refcoal

3.2.1. Important considerations

One of the most important things to consider is the graphitisability of the Refcoal. The effectiveness of the whole process is also important. The following factors could possibly have an influence on the effectiveness:

- *Removal of sodium hydroxide*

  During extraction, NaOH is added as a type of catalyst. Manganyi (2001) studied the diffusion of sodium from Refcoal gel into a leaching solvent (water and DMF). When water was added to the Refcoal solution, Refcoal gel formed by precipitation. It was found that the rate of NaOH diffusion into this water was very fast and the extent of the diffusion increased with a decrease in temperature of the leaching solvent and decreased when the pH was decreased. If direct evaporation of the DMF was done, the

NaOH would not be removed – this could influence the graphitisability of the Refcoal.

- *Recycling of DMF*

  DMF is one of the main reagents during the extraction process and it is therefore important for it to be recycled back into the process. However, it was found that the extent of the extraction was inhibited by the presence of water (Ueckermann, 2004). The recycled DMF must therefore have a minimal water content. The separation of water and DMF could be done via distillation, but the boiling temperatures of water and DMF are close (100°C and 153°C respectively), and therefore the distillation may become expensive if DMF of high purity is needed. The cost of distillation could be reduced by reducing the amount of water used during the recovery of the DMF from the Refcoal solution.

- *Drying of recovered Refcoal*

  After separation of the Refcoal from the Refcoal solution, using precipitation, the final product contains water and this water needs to be evaporated to obtain dry Refcoal. This evaporation process is expensive due to the high amount of energy needed to evaporate water. The Refcoal should therefore contain minimal amounts of water before drying. This is why the densest possible Refcoal gel is needed at the end of the recovery process.

- *Refcoal purification using HCL*

  It is important to achieve the highest possible densities during precipitation and separation to remove as much water and DMF as possible from the Refcoal. Mthembi (2003) developed a process for purifying Refcoal by reducing the inorganic content of the coal. This is done by adding ionic resin and by treating with concentrated hydrochloric acid (HCL). It would be more convenient if the gel was less dense for this process as this would ensure good mixing. However, this factor has to be weighed against the two previously mentioned factors concerning the water content of the DMF and Refcoal.

- *Use of toluene*

  The use of toluene during the precipitation procedure may influence the coking and therefore the graphitisibility of the Refcoal. It is not known, however, whether this would have a positive or negative effect. Toluene may also affect the purity of the Refcoal. It is know that oil agglomerations improve the purity of coals to some extent (Ünal & Aktaş, 2001).

3.2.2. Separation techniques

3.2.2.1. Evaporation

Direct evaporation of DMF from the Refcoal solution is an option, but it may prove expensive due to the amount of energy needed. Also, it has the disadvantage that the product does not form a good mesophase during coking of the Refcoal, thus inhibiting graphitisation in later stages (Kgobane *et al.*, 2002). This method can be considered if graphitisability of the coke is not needed for the specific application. Another concern is that the NaOH in the Refcoal solution stays in the coal after evaporation.

Due to the constraints brought about by evaporation, this separation process was not considered further during this investigation.

3.2.2.2. Precipitation

When water is added to the Refcoal solution, the coal precipitates in a gel form known as Refcoal gel. The temperature of the water has an influence on the recovery of the DMF from the solution (Resenga, 2001). The most important factor in the separation of the Refcoal from the Refcoal solution is the density of the gel that is formed. Centrifugation or filtration can be used to separate the gel from the mother liquor to give a denser gel; this will be discussed in Sections 3.2.2.2.2 and 3.2.2.2.3. Firstly, to be able to work with this Refcoal gel, it is important to know how it will react with its external environment.

3.2.2.2.1. Gels

Tanaka (1981) describes a gel as a form of matter intermediate between a solid and a liquid. It consists of polymers, or long-chain molecules, cross-linked to create a tangled network, immersed in a liquid medium. The interaction of these components has a strong effect on the properties of the gel. The network prevents the liquid from flowing away and the liquid prevents the network from collapsing into a compact mass. Gels are typically soft and resilient (Tanaka, 1981).

Drastic changes in gels can be brought about by small changes in the external environment. Temperature has a major effect on gels: the gel can swell or shrink by a factor of several hundred when the temperature is varied. The pH, electric fields, composition and ionic strength can also have varying effects on gels (Tanaka, 1981; Yung, 2003)

Although the physical chemistry of Refcoal gel is not the same as that of a polymer, it can be expected that is will respond similarly, but not in such extremes. The response of temperature was investigated by Resenga (2001) – a decrease in temperature increased the density of the gel, thereby improving the separation.

These techniques used for the contraction of gels can be used on Refcoal gel to increase its density, thereby expelling more mother liquor, and leading to the more effective removal of DMF.

Additives could therefore have an influence on the gel. The use of oils during the recovery process has been investigated and is discussed in Section 3.2.2.5. To be able to separate the gel from the mother liquor, both centrifugation and filtration are considered.

3.2.2.2.2. Centrifugation

Centrifugal forces are used instead of gravitational force in order to effect separations. The resulting accelerations may be several thousand times that attributable to gravity (Coulson & Richardson, 1999, 365). If particles are to be separated by centrifugation, they must differ either in their density or in their sedimentation coefficient (Hinton & Dobrota, 1976, 24). Refcoal gel has a higher density than the supernatant due to the solid particles it contains, which is why it settles at the bottom after centrifugation.

There are two distinct categories of centrifuges: those that use the principle of filtration and those that use the principle of sedimentation. Both are enhanced by a centrifugal field. They can be further divided into two classes according to the discharge method, which may be batch, continuous or a combination of the two (Coulson & Richardson, 1999: 379). Drying is the most energy-consuming industrial process, and usually uses fuel with a high sulphur content. Therefore, the more liquid that can be separated, the less fuel is used for drying (Palica, 1994). This is one of the main concerns in the Refcoal recovery process. Moreover, the use of either centrifugal decantation or filtration enables the filtrate to be reused. This is an important factor in the Refcoal recovery process because the DMF in the supernatant or filtrate has to be recycled back to the extraction process.

Normal filtration is also a consideration in the recovery process. It has been used in the laboratory as a final means of separating as much water as possible from the Refcoal before drying it.

3.2.2.2.3. Filtration

By using filtration in the process of separating Refcoal from the Refcoal solution, higher densities than with centrifuging could possibly be achieved. It may also be a more practical and cheaper technique. The cost-effectiveness of the methods was not investigated in this study and is therefore not considered when the various techniques are discussed.

The method used for filtration will depend on the properties of the fluid, the properties of the solid, whether it needs to be a continuous or batch process; and the driving force to be used (e.g. gravity, suction, positive pressure, centrifugal forces) (Orr, 1977: 120, 171-172).

Vacuum filtration is an option. It is an improvement on gravitational filtration with regard to the amount of space used and the time used due to the relatively thin filter cake. The cake produced by vacuum filtration will not be as compacted as with higher pressure filtration, but it will have maximum porosity and be uniform in structure, allowing for effective washing. Vacuum filtration can be used for batch or continuous and automatic filtration (Dickey, 1961: 43-49). Although this appears to be a good alternative to centrifugation, the same densities could not be achieved on laboratory scale using a Buchner filter. Therefore pressure filtration was considered.

Pressure filters, unlike vacuum filters, utilise direct liquid pressure to improve flux. Pressure filtration can cause void restriction and therefore flow reduction and stoppage, which outweighs the advantage of the initial higher rate of flux (Dickey, 1961: 84).

The filter cake produced from pressure filtration is a smaller, dryer cake than the wet cake obtained from vacuum filtration. The energy consumption will be significantly lower (Townsend, 2003), and this is exactly what is important when the Refcoal is to be dried.

The filter medium is of considerable importance when designing a filtration system. The choice of filter medium depends on how important the clarity of the filtrate is and what limitations blinding of the filter medium will cause. Also, if the retained solids need to be washed, the most open-textured medium possible should be used (Dickey, 1961: 133). Although the cake is the product of the Refcoal recovery process, the filtrate is also important as it should be recycled back into the process.

Filter aids can be added before filtration to improve it. It is important when using filter aids to ascertain that the alterations caused by them will not be detrimental to the final product, that the cost and time taken will be reasonable, and that the process will be simple (Dickey, 1961: 176; Orr, 1977: 198, 214, 236).

Filter aids could alter the following conditions:

- Viscosity, and therefore the flow rate – this may be altered by temperature or by the addition of liquid
- Solids concentration
- pH
- Coagulation
- Particle precipitation.

These techniques can also be used with centrifugation.

After the filtration process, cake dewatering can be used. The filtrate trapped in the pores of filter cakes can be removed by some mechanical or hydrodynamic means. This will save energy in thermal drying and also improve the handleability of the filter cakes. Mechanical compression brings the particles closer together and squeezes out the excess liquid. Drawing or blowing gas through to displace the retained water is probably the most common method of dewatering a material in the coal industry.

A minimum pressure differential across the cake (entry pressure) is required for the displacement of the liquid by air at the filter cake surface. Once this pressure is overcome, the cake dewaters at a gradually decreasing rate, finally reaching an irreducible moisture level.

The key factors that will determine the level of dewatering are the pore size of the filter cake and the filter medium, and the applied pressure differential (Hosten & San, 2002).

As discussed in this section as well as in Section 3.2.2.2.1, the addition of additives could have an influence on the separation of the Refcoal from the a Refcoal solution by increasing the density of the gel. Oil can also be added to agglomerate the coal and improve the density of the gel.

3.2.2.2.4. Coal agglomeration

Morifi (2002) investigated the addition of oils to the Refcoal gel to expel the water from the gel. Oils were added at the end of the washing procedure, at which stage approximately 1 wt % DMF was retained in the gel. It was found that up to 90 % of the water could be expelled with the addition of toluene.

The addition of oils, especially toluene and tetra-hydro-naphthalene (THN), in the first stage of washing also increased the separation. THN showed better results than toluene, but toluene is a by-product in the coking process of Refcoal and will be cheaper to use. For this reason it has been investigated more intensely (Kitching, 2002).

The addition of oil to the Refcoal gel was compared with the addition of oils to coal slurries. Oil agglomeration is a surface property-based coal-cleaning technique, whereby the separation of the inorganic and organic constituents of coal takes place, due to their surface property differences. The organic constituents are hydrophobic, while the mineral fractions are generally hydrophilic. When a small amount of bridging oil is added to finely ground coal in water and vigorously agitated, agglomeration occurs. The intense agitation breaks the bridging oil into fine spherical droplets. The hydrophobic coal particles form agglomerates of oil-coated particles bonded to other oil-coated particles. The hydrophilic mineral particles remain in the water phase. The agglomerates are then separated from the mineral matter by screening (Ünal & Aktaş, 2001).

The major factors generally controlling the agglomeration process are (Ünal & Aktaş, 2001; Boni & N'kpomin, 1995):

- Particle wetting characteristics
- The amount and type of bridging oil
- The type, concentration and size of the coal
- The amount of volatile matter
- The pH
- The effect of surfactant on agglomeration performance.

Properties such as the density of the bridging oil also have an effect on agglomeration. Better recovery is achieved with lower-density bridging oils (Ünal and Aktaş, 2001). A higher grade and better recovery are achieved with finer coals. Lower-viscosity bridging oils work more efficiently, allowing for the formation of discrete agglomerates (Boni & N'kpomin, 1995). The conditioning time and the agglomeration time have an effect, as well as the stirring rate (Boni & N'kpomin, 1995).

Chapter 4. EXPERIMENTAL

4.1. Apparatus

The following apparatus was used during the experimental procedures.

- Refractive index meter – Carl Zeiss 51662 made in Germany
- Centrifuge (1) – LKB Bromma 2160 Midispin, with a fixed rotator at an angle of 45° and a 120 mm inner radius, using 110 mℓ tubes and rotating at ±13 000 r/min.
- Centrifuge (2) – Model PR-2 centrifuge, with a swing-out rotator and a radius of approximately 160 mm, using 200 mℓ glass bottles and rotating at ±2 000 r/min
- Centrifuge (3) – IEC Model K centrifuge, with a swing-out rotator and a radius of approximately 200 mm, using 1 000 mℓ bottles and rotating at ±4 500 r/min
- Centrifuge (4) – Clement GS 150 centrifuge, with a swing-out rotator and a radius of approximately 170 mm, using 10 mℓ tubes and rotating at ±3 200 r/min.
- Mixer – Highdolph RZR1 with a speed of 35-250/280-2200 ℓ/min using a setting of ±5 out of 10.
- Mixer – Aero-whip from Glomail products
- Labtex Chiller and Labcom CPE 50 heater and temperature controller
- Karl Fischer titration apparatus with a Metrohm 787 KF Titrinon and a 703 Ti stand, using hydranal composition 5 as reactant, together with analytical-grade methanol
- Spectrophotometer – Ultraspec II, using 600 nm for measurements
- Refcoal jacketed reactors, 1 and 3 ℓ
- Pressure filter, using pressures between 100 and 600 kPa.

Figure 4.1.1 shows the layout of the jacketed reactor used to produce the Refcoal extract and Figure 4.1.2 the pressure filter used for the separation experiments.

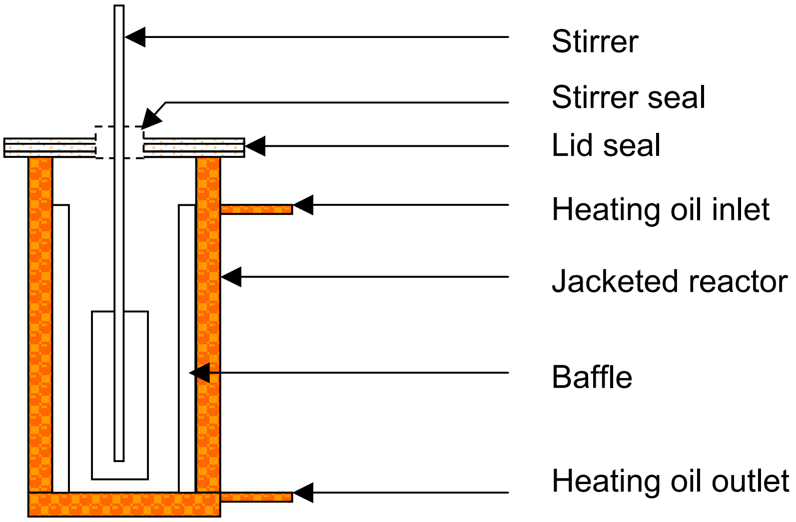


Figure 4.1.1: Jacketed reactor used for the production of Refcoal extract

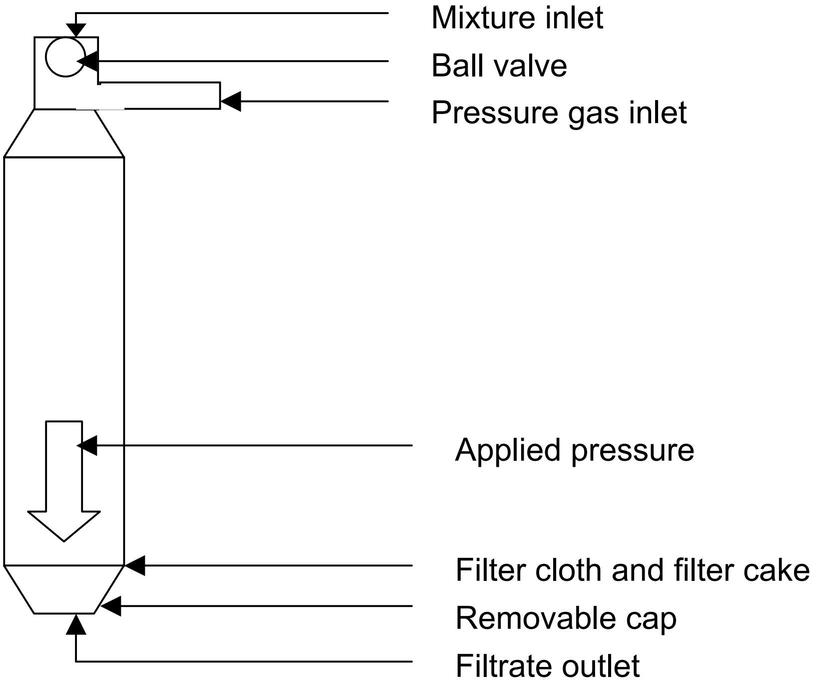


Figure 4.1.2: Simplified diagram of pressure filter used

4.2. Raw Materials

The following raw materials were used during the experimental procedures:

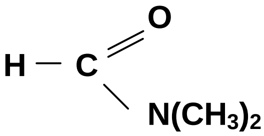
Dimethylformamide (DMF) (BASF, 2000)

DMF is a clear, high-boiling, low-volatility, polar, hygroscopic liquid with a faint, characteristic odour. It is freely miscible in water, alcohols, ethers, ketones, esters, and chlorinated and aromatic hydrocarbons. It is either immiscible or only partially miscible with aliphatic hydrocarbons. DMF is an aprotic solvent with a high dielectric constant.

Even at elevated temperatures, aqueous solutions of DMF have little tendency to hydrolyse. However, the addition of acids or bases accelerates hydrolysis to formic acid and dimethylamine.

DMF is also known as “N,N-Dimethylformamide” and “Formic acid dimethylamide” and has the following molecular formula and structure:

C_3H_7ON



DMF has a boiling range of 152.5 – 153.5°C at 1.013 bar and a density of 0.948 – 0.952 g/cm^3.

DMF is regarded as "possibly carcinogenic to humans" and it is recommended that the time-weighted average exposure be no more than 10 ppm of DMF vapour or 30 mg/m^3 in air by weight for an 8-hour day (Othmer, 1979, *11:* 974).

Dimethylacetamide (DMAC)

DMAC is a colourless, high-boiling polar solvent. It is a good solvent for a wide range of organic and inorganic compounds and is miscible with water, ethers, esters, ketones and aromatic compounds.

The rate of hydrolysis of DMAC is very low, but increases somewhat in the presence of acids or bases. In the absence of water, acids or bases, DMAC is stable at temperatures up to its boiling point at atmospheric pressure. Its greater stability allows more economical recovery by distillation relative to that of other similar solvents.

DMAC has a boiling point of 166.1°C, a melting point of -20°C, a vapour pressure of 0.27 kPa at 25°C and a density of 0.945 g/mℓ at 15.6°C.

In any 8-hour work shift of 40 hours a week, DMAC should not exceed a time-weighted average of 10 ppm of DMAC vapour in air by volume or 35 mg/m^3 in air by weight (Othmer, 1979, *1:* 162).

Tshikondeni Coal (Morgan, 2000)

The coal, obtained from Tshikhondeni mine in Limpopo Province, South Africa, was assumed to have the composition stated in Table 4.2.1.

Table 4.2.1: Composition of Tshikondeni coal

Proximate analysis	%	Ultimate analysis (d.a.f)	%
Moisture (air dry)	0.6	Carbon	90.2
Ash (dry basis)	9.0	Hydrogen	4.8
Volatile matter (dry basis)	23.3	Nitrogen	2.1
Fixed carbon (calculation, dry basis)	67.4	Sulphur	0.7
Total sulphur (dry basis)	0.85	Oxygen (by difference)	2.2

Water

Distilled water was used throughout all the experiments.

Toluene

Toluene is a clear, colourless, aromatic hydrocarbon liquid of characteristic odour. The material is derived from petroleum sources and has a low sulphur content. Toluene is almost completely immiscible with water, but is completely miscible with castor, linseed and other oils, as well as with most organic liquids (Protea Industrial Chemicals, 2004). Toluene has a boiling point of 110.8°C (Perry & Green, 1998: 2-46).

4.3. Planning

Centrifugation and filtration were investigated as separation processes. Direct evaporation was not considered, as discussed in Section 3.2.2.1.

4.3.1. Techniques investigated

The following techniques were investigated when using water to precipitate out Refcoal gel:

- The effect of the amount of wash water used
- The effect of stirring time
- The effect of centrifugation time
- The effect of the wash water temperature
- The effect of syneresis (the separation of liquid from a gel that is caused by contraction)
- The effect of pH change
- The effect of oil agglomeration
- The effect of using a different organic solution, dimethylacetamide (DMAC).

Counter-current washing was also briefly investigated.

4.3.2. Ranges investigated

- For the amount of wash water used, mass ratios of water to Refcoal solution (or Refcoal gel) from 0.2:1.0 to 1.2:1.0 were used. These ratios were chosen because the gel becomes too thick to operate with at lower water amounts, and at higher water amounts it becomes uneconomical.
- Stirring times ranged between 1 and 10 min. Shorter times gave insufficient mixing and longer times would be uneconomical.
- Centrifuging times ranged between 10 and 25 min. Kitching (2002) found that the best centrifuging time was 20 min and therefore a range around this was chosen to confirm his results.
- Wash-water temperatures of ±0°C and room temperature were used. Resenga (2001) had investigated this, and therefore it was only a confirmation of her results.

- Syneresis temperatures ranged between room temperature and 80°C. At higher temperatures, water starts to evaporate too fast and causes drying to take place and not syneresis.
- The pH of the wash-water was either very low (pH=1) or intermediate (pH=2.5). A normal distilled water experiment was used as a reference.
- For oil agglomeration (gel agglomeration), toluene was used as the oil from 0 % to 500 % (based on the mass of solids in the Refcoal solution/gel).
- Dimethylacetamide (DMAC) was used as organic solvent to extract the coal. Normal washing was done with mass ratios of water to Refcoal solution/gel of 0.2:1.0 to 1.2:1.0. The purpose was to allow this solvent to be compared with the DMF used in the standard experiments.

4.4. Calibrations

Refractive indices were used for determining the amount of DMF, toluene and water in the solution expelled from the Refcoal gel.

4.4.1. Refractive index calibration for the water-DMF system

This system was used in experiments where only distilled water was used as wash water. Samples of water and DMF with different concentrations were made up. The refractive indices of these samples were measured at 25°C and recorded. A calibration curve was drawn up and a trend-line was fitted to give an equation for estimating the concentration of DMF. This is shown in Figure 4.4.1.

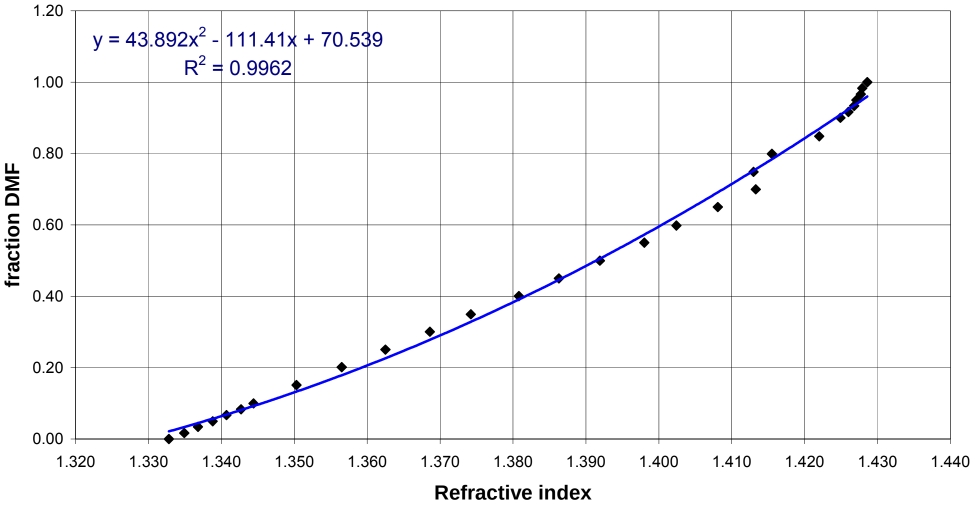


Figure 4.4.1: Refractive index calibration for a DMF-water system

4.4.2. Refractive index calibration for water-DMF-toluene system

A ternary diagram for a water-DMF-toluene system was developed using the procedure described by Stead & Stead (1990). The experiments were done at 20°C, taking refractive index measurements at 25°C. Figure 4.4.2 shows the refractive index relationship between toluene and water. Figure 4.4.3 shows a ternary diagram of a DMF-water-toluene system, also containing the tie-lines. These graphs were used to calculate the concentrations of water, DMF and toluene in the experiments where toluene was added at the beginning of the wash procedure.

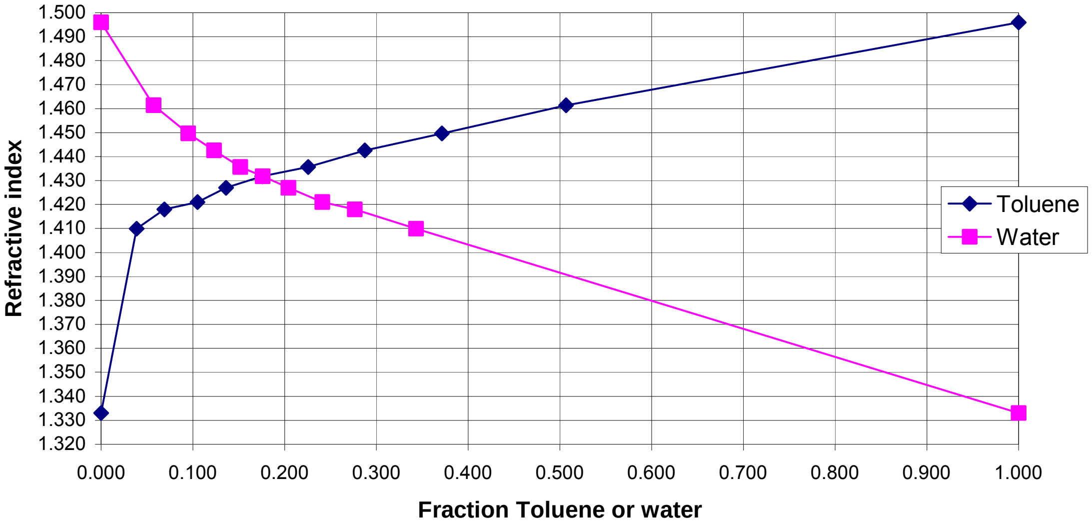


Figure 4.4.2: Refractive index relationship of toluene and water

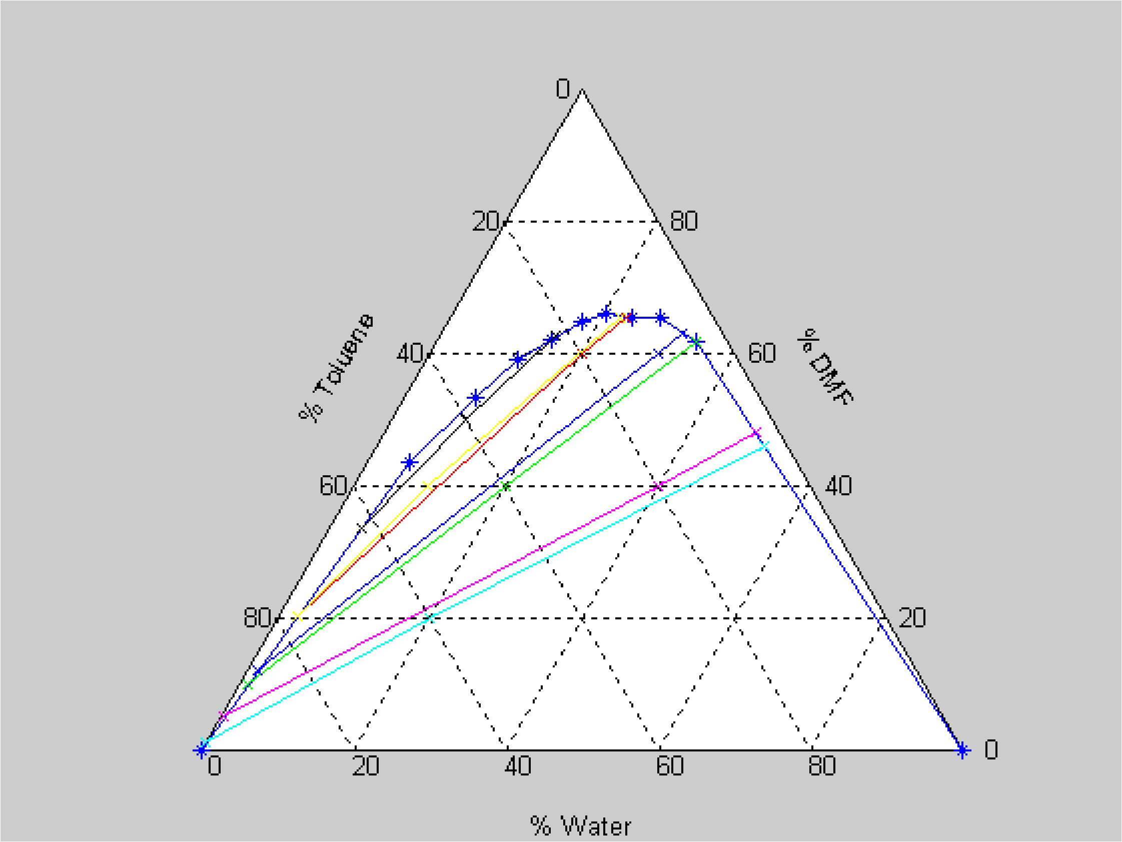


Figure 4.4.3: Ternary diagram for a DMF-water-toluene system

4.5. Preparation of Refcoal Solution

The Refcoal extract is prepared in a jacketed reactor, shown in Figure 4.1.1. For a 1 ℓ reactor, 80 g of coal, 800 g of DMF and 8 g of NaOH is used. Firstly, the reactor is heated up to 90-95°C. While this is happening, the coal and

DMF are added to the reactor and stirred under a nitrogen atmosphere. When the reactor reaches 90°C, the NaOH is added and the extraction commences. The extraction takes about six hours, but with efficient mixing the time can be reduced to four hours.

During the extraction, samples of approximately 2 mℓ are taken and centrifuged (using centrifuge 4, for 3 min). A portion of the top layer, 0.10 g, is measured into a 50 mℓ volumetric flask, and this flask is then filled with DMF. The absorbance of this liquid is taken, using a spectrophotometer at 600 nm. When an absorbance of approximately 1.05 is reached, the extraction is stopped.

The Refcoal extract is then decanted into a 1 ℓ centrifuge bottle and centrifuged for one hour (using centrifuge 3). The Refcoal solution was decanted from this bottle into another sealed bottle and allowed to cool before it was used in the experiments described below.

The same procedure is followed when a reactor temperature of 135°C is used. The ratio of DMF:coal:NaOH becomes 100:20:2 or 100:30:3. The time for the extraction is approximately three hours. The solids mass can range between 10 and 20 wt %.

The mass of solids in the Refcoal solution is determined by washing the solution with water and so precipitating out a Refcoal gel by centrifugation. The wash is repeated until the DMF concentration is below 1 wt %. This gel is then filtered to extract the excess water and dried in an oven at 60°C overnight in a nitrogen atmosphere. The solids are then measured. For an absorbance of approximately 1.05, a solids mass of ±8 wt % is achieved.

4.6. Precipitation Experiments

4.6.1. Separation by centrifugation

4.6.1.1. General experimental procedure

The general procedure used during separation by centrifugation is described below. There were small variations in other procedures, which will be discussed in the following sections.

Refcoal solution (RCS) produced at 95°C or 135°C is used. The amount of RCS to be used is measured into a centrifuge tube or holder, after which water, at room temperature, of a specific quantity or ratio is added. This is then mixed for 1 min (using high-shear mixing) and centrifuged for 20 min at a relative centrifugal force (RCF) of ±20 000 (times gravitation). After centrifuging, the supernatant is decanted and clean water with a certain ratio to the Refcoal gel (RCG) is added, mixed and centrifuged. This is continued for the number of stages the specific experiment requires. The masses of the RCS, water, RCG and supernatant are recorded, as well as the refractive index of the supernatant. Using these values, a mass balance over the system can be calculated.

4.6.1.2. The effect of the amount of wash water used

The amount of water used to precipitate the RCG was investigated within the range of 0.2:1.0 to 1.2:1.0, where the mass ratios are of water to RCS or RCG. The washing procedure was repeated 8 to 11 times, depending on the quantity of water used. The water added to the RCG was added in ratios due to the mass loss during stirring.

The Refcoal solution made, at 95°C and 135°C RCS, was used in the experiments. The results of these experiments are given in Section 5.2.1.

4.6.1.3. The effect of stirring time

The general washing procedure was used and the stirring times were varied between 1 and 10 min. A water to RCS or RCG ratio of 0.6:1.0 was used with the RCS made at 95°C. The results of these experiments are given in Section 5.2.2.

4.6.1.4. The effect of centrifugation time

The general washing procedure was used but the centrifuging time was varied between 10 and 25 min. Water to RCS or RCG ratios of 0.6:1.0 and 1.0:1.0 were used with the RCS made at 95°C. The results of these experiments are given in Section 5.2.3.

4.6.1.5. The effect of the wash water temperature

The general washing procedure was used. Water to RCS or RCG ratios of 0.2:1.0 to 1.2:1.0 were used. Water at room temperature and at 0°C was used. Higher temperatures were not used because Resenga (2001) found that higher temperatures did not give good separation. RCS made at 95°C was used. The results of these experiments are given in Section 5.2.4.

4.6.1.6. The effect of syneresis

It was found that if the RCG was left in an enclosed container for some time, then syneresis took place. Supernatant was expelled from the gel, causing the gel to shrink and thereby removing DMF from the gel.

The general washing procedure was used, but only the first wash was undertaken. A water to RCS ratio of 0.4:1.0 and 0.6:1.0 was used. Different percentages of toluene were added at the beginning of the wash, ranging from 0 wt % to 120 wt % (on the basis of the mass of solids in the RCS). After the first washing, the gel was enclosed in containers to prevent evaporation from taking place. These containers were placed in an oven, for two or three hours, at temperatures ranging from room temperature to 80°C. After the required time had elapsed, the expelled supernatant was decanted and all the related masses were measured to calculate the mass change of the gel. The solids concentration in the gel wash was calculated by drying a specific mass of gel in a nitrogen atmosphere overnight at approximately 60°C.

The syneresis results are given in Section 5.2.5.

4.6.1.7. The effect of pH changes

The standard washing procedure was used. A water to RCS or RCG ratio of 0.6:1.0 was used. Wash water with pHs of 0.9, 2.4 and 5.5 (standard distilled water) was used. The pHs were achieved by adding 32 % HCL. RCS made at 95°C was used. As usual, the different masses were recorded, as well as the pH of the solutions. The results are given in Section 5.2.6.

4.6.1.8. The effect of gel agglomeration

4.6.1.8.1. Toluene added at the end of washing

The standard washing procedure was used. RCS made at 95°C was used and was washed with large amounts of water until only 0.5% DMF was left in the RCG. Toluene of 70 to 500 wt % was added on a mass basis of solids to the final RCG. Between 70 and 130 wt %, only gentle stirring for 1 min was used; in the other experiments, high-shear mixing was used until agglomeration took place (an average of 5 min). The mixture was then centrifuged and the appropriate measurements were taken. The results are given in Section 5.2.7.1.

4.6.1.8.2. Toluene added at the beginning of washing

The standard washing procedure was used. Water to RCS or RCG ratios of 0.2:1.0 to 0.6:1.0 were used. The percentage toluene added was calculated on a mass basis of the amount of solids in the RCS. When RCS made at 95°C is used, it is assumed that the RCS has 8 wt % solids and 92 wt % DMF, ignoring the small amount of NaOH present. The results are given in Section 5.2.7.2.

4.6.1.9. The effect of using dimethylacetamide as coal solvent

Dimethylacetamide (DMAC) is a more expensive material than DMF, but it is less toxic. Its use would therefore be more environmentally friendly (Othmer, 1979; Morgan, 2004). The boiling point of DMAC is also higher than that of DMF and therefore separation from water requires less energy. Better separation would motivate the use of DMAC.

The standard washing procedure was used. RCS made at 95°C was used and instead of using DMF as extraction solution, DMAC was used. Water to RCS ratios of 0.2:1.0 to1.2:1.0 were used. The results are given in Section 5.2.8.

4.6.2. Separation by filtration

4.6.2.1. General experimental procedure

Vacuum filtration has been used in the laboratory, but a cake of sufficient density could not be achieved. Centrifuging gave much denser gels. Pressure filtration was therefore used for further studies. RCS produced at 95°C was poured into a glass beaker, and water of a specific ratio was added. This was mixed and poured into the pressure filter. Pressure up to 600 kPa (g) was applied until breakthrough was achieved. The filter cake was removed, the same ratio of water was added to it, and it was then mixed and filtered again. Depending on the experiment, the procedure was repeated up to four times. Due to the loss of material during transfer, no complete washes could be done. All masses were recorded. Figure 4.1.2 shows a simplified diagram of the pressure filter used.

4.6.2.2. The effect of the amount of wash water used

Ratios of 0.2:1.0 to 0.6:1.0 of water to RCS or RCG were used. The time for which the pressure was applied and the amount of pressure applied depended on the quantity of mixture and therefore on the thickness of the cake. The maximum applied pressure was 600 kPa(g) and the minimum approximately 100 kPa(g). The results are given in Section 5.3.1.

4.6.2.3. The effect of gel agglomeration

A ratio of 0.6:1.0 of water to RCS or RCG was used. As with the agglomeration during centrifuging, the percentages of toluene were based on the mass of solids in the RCS. Toluene of 0 % to 120 % was used. Toluene was added to the RCS before the addition of water. The time for which the pressure was applied and the amount of pressure applied depended on the quantity of mixture and therefore on the thickness of the cake. The maximum applied pressure was 600 kPa(g) and the minimum approximately 100 kPa(g), depending on when breakthrough occurred. The results are given in Section 5.3.2.

4.6.3. Counter-current washing

4.6.3.1. Calculations and procedure

4.6.3.1.1. Preparation of calculations

Counter-current washing was done using RCS produced at 95°C. Water to RCS ratios of 0.4:1.0 to 0.8:1.0 were used. Figure 4.6.1 shows a schematic layout of the counter-current washing process.

The number of experimental stages to begin with is calculated from equation 1:

$$(1-n)^x \leq 0.01 \qquad (1)$$

Where

n = the recovery of DMF for the first stage of normal washing (the fraction DMF in the supernatant after the first wash)

x = the number of stages

0.01 = the required 1% of DMF remaining in the RCG in the final stage (RCG_x).

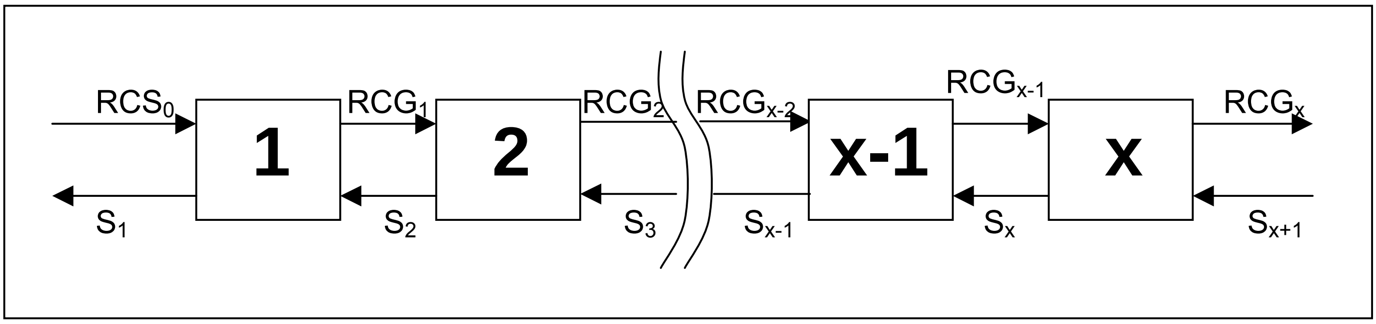


Figure 4.6.1: Schematic layout of a counter-current washing process

For the water to RCS ratio of 0.8:1.0, seven stages, for 0.6:1.0 nine stages and for 0.4:1.0 thirteen stages are calculated.

The counter-current calculations for a water to RCS ratio of 0.8:1.0 are done first. Therefore if 100 g of RCS enter stage 1, 80 g of water will enter stage 7.

The following assumptions were made:

- There are 92 wt % DMF and 8 wt % solids in the RCS; this can be verified from drying tests.
- All the solid particles stay in the RCG phase. In industry this would be a closed system and minor losses of solids would take place. Precautions, such as filters, could be used to prevent losses.
- For the first calculations, 75 wt % of the water that enters stage 7 in S_8 will exit stage 7 in the RCG_7. The validity of this statement was unknown, but the correct concentration was experimentally determined through repetition until equilibrium was reached.
- There is 1 % DMF in the RCG_7. This is an estimated concentration that will not have an influence on the graphitisability of the coke manufactured from the Refcoal (as discussed in Section 2.2.3).
- The RCG mass decreases constantly from the RCS_1 mass to the RCG_7 mass. The validity of this statement was unknown, but the correct mass change was experimentally determined though repetition until equilibrium was reached.

Equation 2 is used to calculate the mass of DMF left in the RCG_1 after the first stage.

$$C_{DMF,RCG,1} = \frac{C_{DMF,RCG,x}}{(1-n)^{x-1}} \qquad (2)$$

where $C_{DMF,RCG,x}$ is the concentration of DMF left in the RCG_x.

Now the mass balance over the whole system can be calculated.

For the experiment, all the calculated solutions ($S_1 \ldots S_{x+1}$) are prepared. S_2 is added to the Refcoal solution (RCS_0), mixed for 1 min (with a high-shear mixer) and centrifuged for 20 min with an approximate RCF of ±20 000 (times gravitation). The supernatant (S_1’) is decanted, and the refractive index of the supernatant is measured, as well as all the applicable masses. The RCG_1 is then washed with solution S_3 in stage 2, following the same procedure as with stage 1. This is then repeated up to stage x.

The measured data are then used to calculate a new mass balance and the experiment is repeated. This is done until equilibrium is achieved between the measured and calculated values. For example, the calculated S_1 and the real S_1' should have the same masses and concentrations.

The results are given in Section 5.5.

4.6.3.2. Gelling tests

The use of a DMF-water mixture to gel the Refcoal solution (RCS_0) can cause problems. When the mixture contains too much DMF, the RCS will not gel and therefore the process will not be initiated. This was found to be the case during the counter-current experiments with water to RCS ratios of 0.6:1 and 0.4:1.

Experiments were done to determine a relationship between the concentration of water and DMF in the gelling solution (S_2) and the time for gelling to take place, also if separation took place after centrifuging.

Different concentrations of water and DMF were added to the RCS, as well as different quantities of solution. These were thoroughly mixed and left to gel. The time that they took to gel was recorded. If gelling took place, the gel was centrifuged and the supernatant decanted. The related masses were recorded.

The results are given in Section 5.5.3.

Chapter 5. RESULTS AND DISCUSSION

Note: Concerning the graphs in the figures – the points are connected to provide clarity and are not for interpolation.

5.1. Refractive Index Calibrations

5.1.1. Water-DMF system

The calibration curve for the water-DMF system can be seen in Figure 4.4.1. It was found that refractive index measurements were not accurate enough to use for detailed mass balances. This is possibly due to some of the organic materials dissolved in the DMF in the supernatant, especially in the first stages of washing when more yellow than colourless supernatant was observed. Components such as toluene, benzene, pyridine, quinoline, etc. have higher refractive indices (1.496, 1.501, 1.510, 1.627 respectively) than DMF and water (1.431, 1.333 respectively) and could increase the total refractive index measurement. This results in a higher amount of DMF in the supernatant being calculated, causing the mass balance to be inaccurate. The amounts of DMF in the supernatant, in the last stages of washing, become “negative”, although the physical refractive index measurement shows differently. This suspicion was confirmed when the percentage of water in the supernatant was measured with Karl Fischer titration – in the first stages, the amount of DMF was lower than that measured with the refractive index meter.

Due to the extreme expensiveness of the Karl Fischer titration procedure, this method was not used to determine the concentrations. The theoretical calculation of the amount of DMF and water in the supernatant was used, under the assumption that the ideal mixing had taken place. This means that the ratio of water and DMF in the supernatant will be the same as in the gel.

Figure 5.1.1 shows how the refractive index calculation, the Karl Fischer titration and the theoretical results differ. The graph shows the mass % of DMF left in the RCG after the washing stage, calculated using equation 3.

$$C_{DMF}\% = \frac{M_{DMF,RCG}}{M_{DMF,RCS}} \times 100 \qquad (3)$$

Where

$M_{DMF,RCG}$ = mass of DMF left in the gel after washing

$M_{DMF,RCS}$ = total mass of DMF in the RCS.

Water to RCS or RCG ratios of 0.4:1.0 and 0.6:1.0 were used for this experiment.

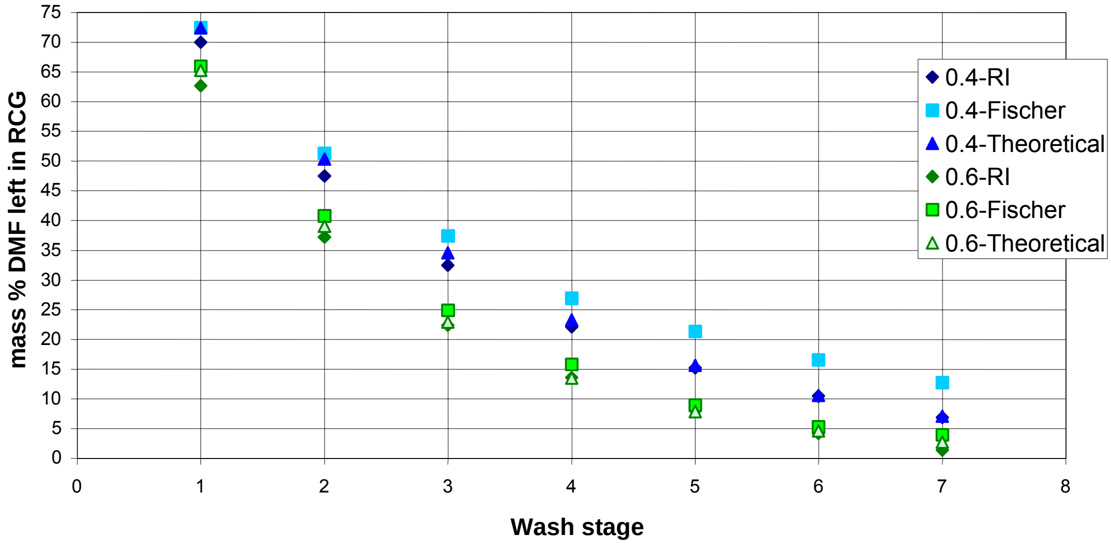


Figure 5.1.1: Graph showing the results obtained using the refractive index calculation, Karl Fischer titration and theoretical calculations

The difference in the Karl Fischer titration and the refractive index calculation results can be used to determine roughly the amount of organic materials that is removed with the supernatant in the first stages of the wash. If the concentration of organic materials is too high, it could have an influence on the separation of the water and DMF via distillation. Table 5.1.1 gives a rough calculation of the amount of organic materials in the supernatant after the RCS has been washed with a ratio of 0.4:1.0 (water to RCS). It is assumed that the results from the Karl Fischer experiment are correct. The difference in the amount of water calculated from the refractive index and the results of the Karl Fischer experiment gives the amount of organic materials that is dissolved in the supernatant of the first wash.

Table 5.1.1: Calculation of organic materials dissolved in supernatant

	Concentration Water (g/g)	**Concentration DMF (g/g)**	**Dissolved organic materials (g/g)**
Refractive index	0.241	0.759	0
Karl Fischer	0.304	0.633	0.063
Difference	*0.063*	*0.096*	*-0.063*

For a 0.6:1.0 water to RCS ratio, a concentration of approximately 0.058 (g/g) organic materials is present in the supernatant after the first wash.

The total amount of organic materials in the water-DMF mixture to be distilled is dependent on the amount of supernatant expelled. This in turn is dependent on the density of the gel that is formed and therefore on the process efficiency that was investigated in this study.

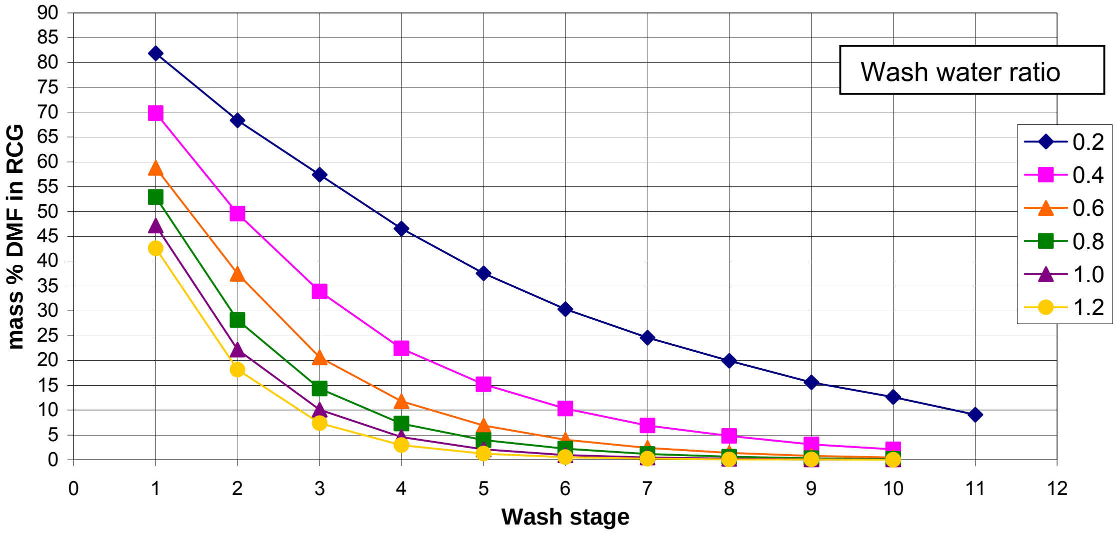
The effect of the organic content in the supernatant (which remains in the DMF-water solution), on the separation of the DMF from the water via distillation should be evaluated.

5.1.2. Water-DMF-toluene system

It was decided not to use the ternary diagram due to the inaccuracies described in Section 5.1.1. It was assumed that the ratios of DMF, water and toluene in the RCG and the supernatant were the same. Theoretical calculations were therefore done, as discussed in the following sections.

5.2. Separation by Centrifugation

5.2.1. The effect of the amount of water used



The more water used, the more DMF could be removed from the RCG. Figure 5.2.1 shows the mass % of DMF remaining in the RCG after each stage of washing, using RCS made at 95°C, calculated using equation 3.Figure 5.2.1: The effect of the amount of water used on the mass % of DMF left in the RCG (RCS made at 95°C)

As seen in Figure 5.2.1, the plot of the 0.2:1.0 and 0.4:1.0 water to RCS or RCG ratios does not follow the same pattern as the rest. When the 0.2 and 0.4 water ratios are added to the RCS, they form a much thicker gel than with the other water ratios. Also, with centrifuging the gel retains more liquid than with the other water ratios. Therefore less supernatant is expelled in relation to the other water ratios and so less DMF is removed.

Figure 5.2.2 shows how the mass % of DMF differs when using RCS made at 95°C and 135°C.

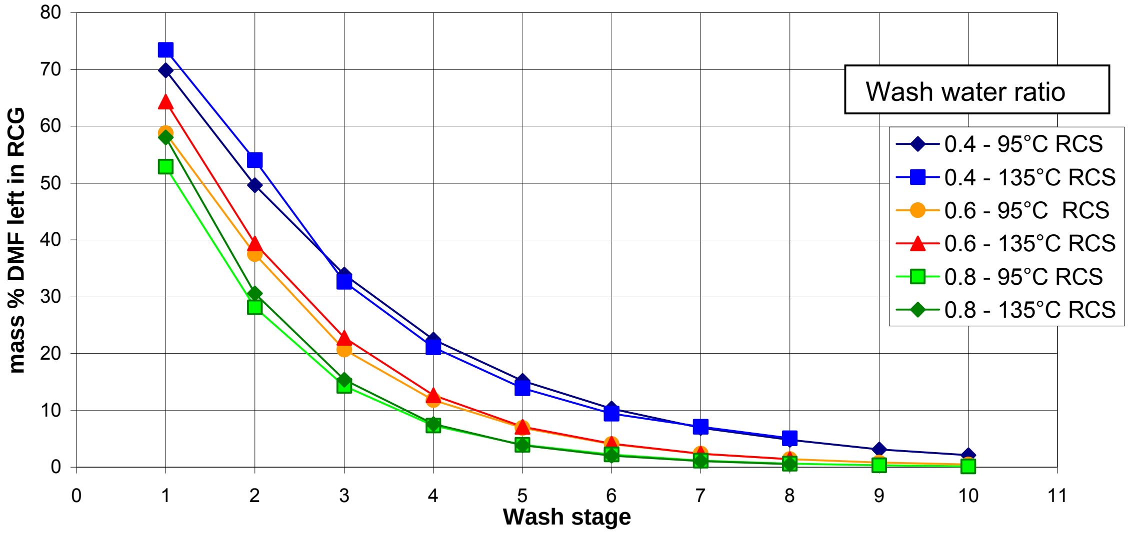


Figure 5.2.2: Difference in % DMF with the use of RCS made at 95°C and 135°C with different wash water ratios

There is some difference in the mass percentages of DMF left in the RCG of the RCS made at 135°C and 95°C, especially in the first few stages. One would have expected that the removal of DMF from the RCS made at 135°C would be quicker because of the higher amount of solids in the 135°C RCS (±15 wt %) than in the 95°C RCS (±8 wt %), but this is not the case. On the contrary, the removal is lower than or the same as with the 95°C RCS. This may be due to the amount of solid particles in the RCS. The higher amount of solids causes a more swollen and stable gel to form, and this stable gel expels less supernatant on centrifuging, and removes less DMF.

Figure 5.2.3 shows the solids fractions in the washed RCG at different stages of the different water ratios used.

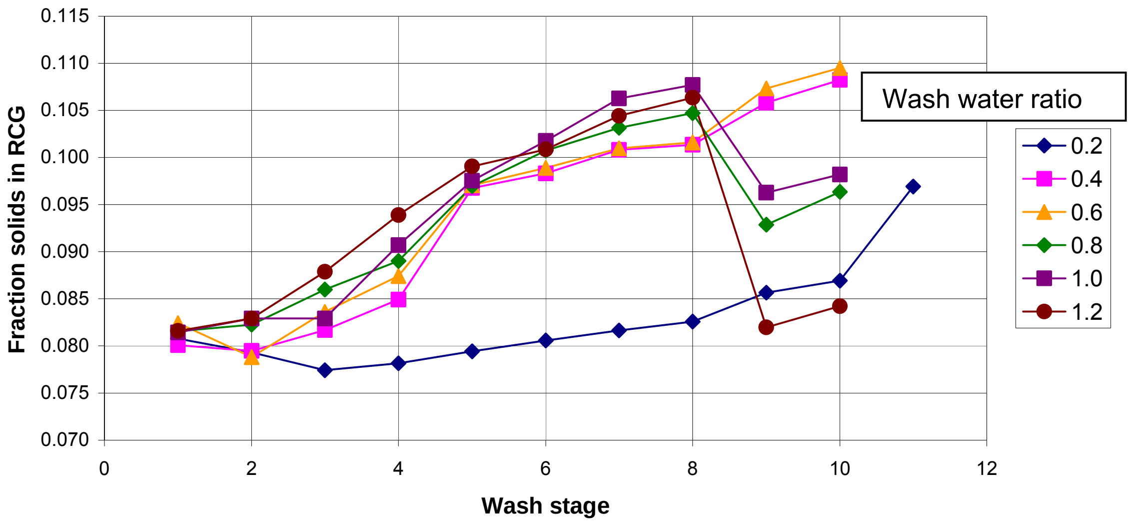


Figure 5.2.3: Solids fractions in the RCGs at the different stages of washing, using different ratios of water

An increase in solids is observed in each stage. Also, when more water is used, the amount of solids is greater. This happens up to stage 8, after which the fractions of solids drop in the 0.8, 1.0 and 1.2 water ratios used.

When the experiment was being done, it was observed that some of the solid particles floated on the supernatant after centrifugation. Theoretically, the solid particles would be denser than the supernatant and should not float. However, during the mixing process, using higher amounts of water, air bubbles were observed. The lower concentration of solids (less-dense gel) is therefore due to the air bubbles driving the solids to the surface of the supernatant.

The use of baffles could prevent this decrease in gel density. The baffles will give more uniform mixing, thereby decreasing the ingress of air into the mixture.

5.2.2. The effect of stirring time

Figure 5.2.4 shows that with prolonged stirring, less DMF is removed. This is due to less-dense gels forming after centrifugation when prolonged stirring is used. As explained in Section 5.2.1, stirring can cause air bubbles to push solids to the surface of the supernatant, giving a less-dense gel. When the mixture is stirred longer, more air is mixed into the gel, lowering the density.

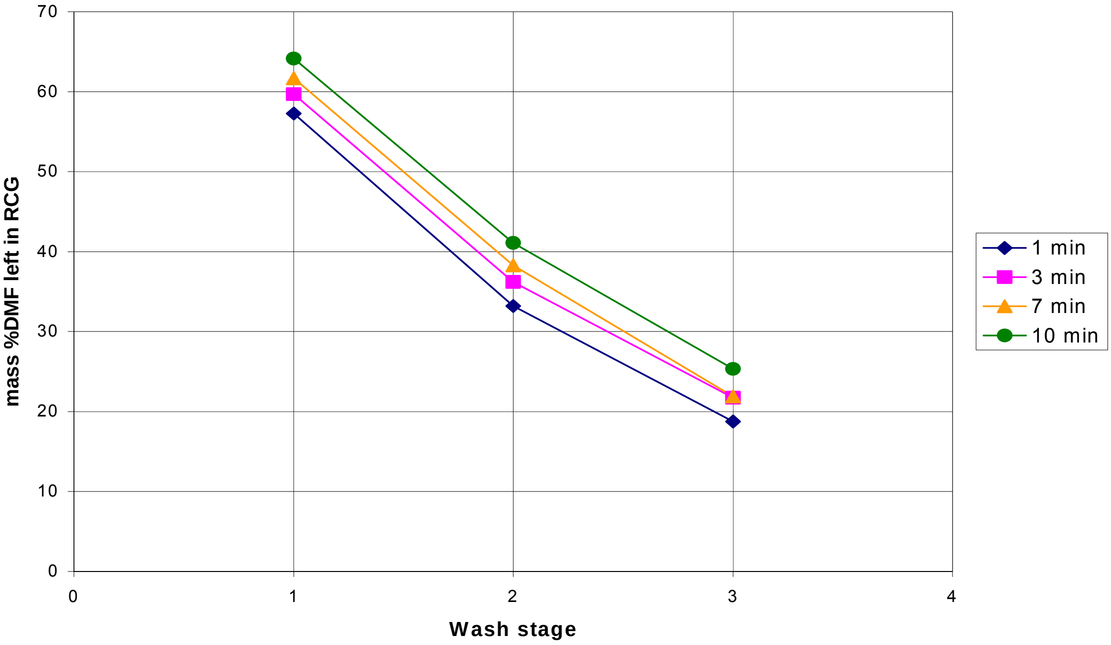


Figure 5.2.4: The effect of stirring time on the removal of DMF from RCG

5.2.3. The effect of centrifuging time

Figure 5.2.5 shows the effect of the centrifuging times on the removal of the DMF.

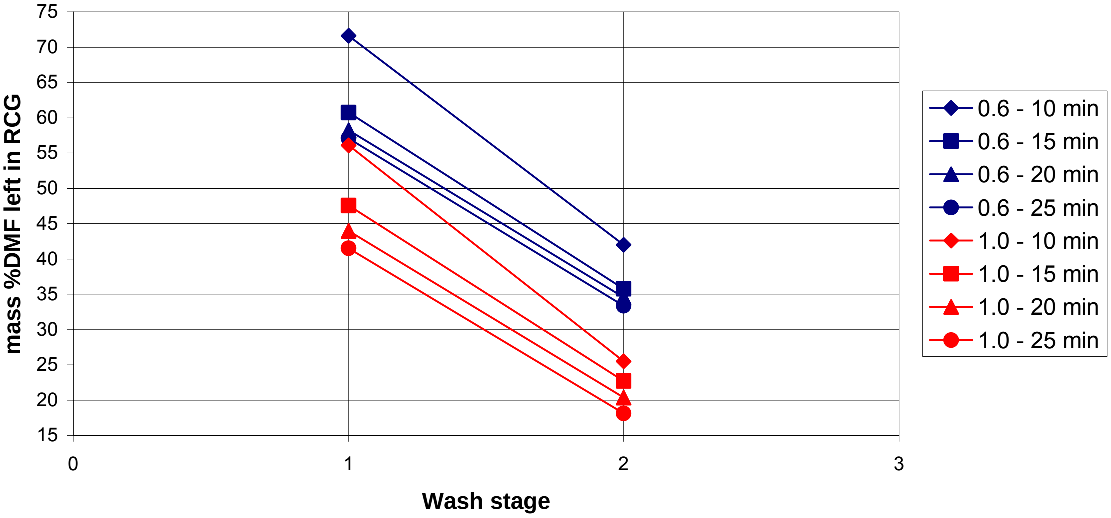


Figure 5.2.5: The effect of centrifuging time on the removal of DMF from RCG

More efficient separation is observed with longer centrifugation. This is due to the force being applied for a longer time. At 25 min, the difference in time has less of an effect. This is because the gel reaches a maximum density and further applied force will not increase it.

5.2.4. The effect of wash water temperature

Figure 5.2.6 shows the effect that the temperature of the wash water has on the separation of DMF from the RCG, using RCS made at 95°C. Only the water to RCS or RCG ratios of 0.4:1.0 to 0.8:1.0 are shown, but the other ratios show similar results.

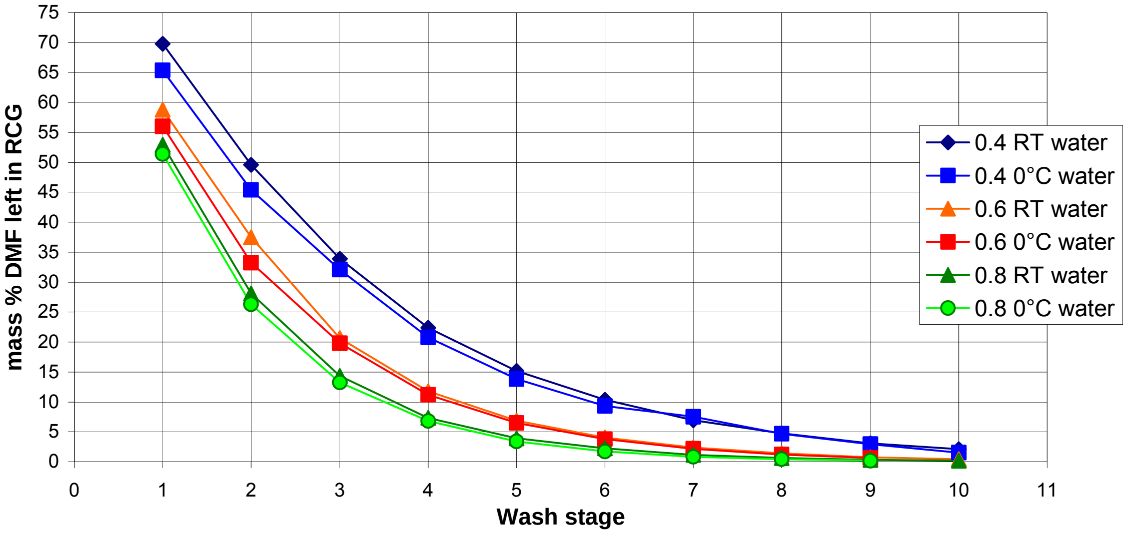


Figure 5.2.6: The effect of the wash water temperature and ratio on the removal of DMF from RCG made at 95°C

The cold water gives somewhat denser RCGs on centrifuging and therefore improves the separation by approximately 5% in the first stages when RCS made at 95°C is used.

The gel becomes more dense and structured when colder. At cooler temperatures, the coal matrix, which keeps the mother liquor in place, contracts and expels more liquid. This then gives better separation.

5.2.5. The effect of syneresis

When RCS was washed once with water, at a ratio of 0.6:1.0 (water:RCS) and with the addition of 120 % toluene, a total of 20 % solids was achieved in the gel. Before syneresis the gel contained 12.5 % solids. Therefore an increase in solids of 7.5 % was achieved. This low-effort and low-cost procedure could be used to increase the gel density between washing stages, thereby improving the washing efficiency at low cost.

During the syneresis test, it was observed that the heating of the gel caused a more liquid gel to form. After centrifuging the gel density increased, and after mixing with a spatula the gel broke up again. But no supernatant was expelled during centrifuging. This result is not understood at present, but it could help with the separation process if the gel is easier to break down. Filtration could be used as a separation technique when the gel has been broken down.

5.2.6. The effect of the pH of the wash water

The reaction between HCL and NaOH in the RCS was not taken into consideration during mass balancing, due to the small amounts added. A gel with a low pH (pH=1) and a gel with a high pH (pH=11) did not show a significant difference in the separation of DMF from the gel.

5.2.7. The effect of gel agglomeration

5.2.7.1. Toluene added at the end of washing

Adding toluene to the clean RCG caused the RCG to agglomerate and after centrifuging, the mixture formed three layers. A dark bottom and top layer and a clear middle layer containing some dark particles were observed. When 70%-130% toluene was added with gentle stirring, the improvement in the solids concentration in the gel was not very good, as seen in Table 5.2.1. The reason why the percentage of solids in the agglomerate of the 110 % toluene experiment was lower than in the other experiments could be because a lower stirring energy was used. Stirring energy has a considerable effect on the agglomeration. When 70 % toluene was used with high-shear mixing, as shown in Figure 5.2.7, 30 % solids were obtained, compared with 16 % when gentle stirring was used.

Table 5.2.1: Effect of the addition of toluene to RCG with gentle stirring

% Toluene added	**70**	**90**	**110**	**130**
% Solids in gel	9.9	9.9	9.9	9.9
%Solids in agglomerate	16.2	16.3	15.6	18.7

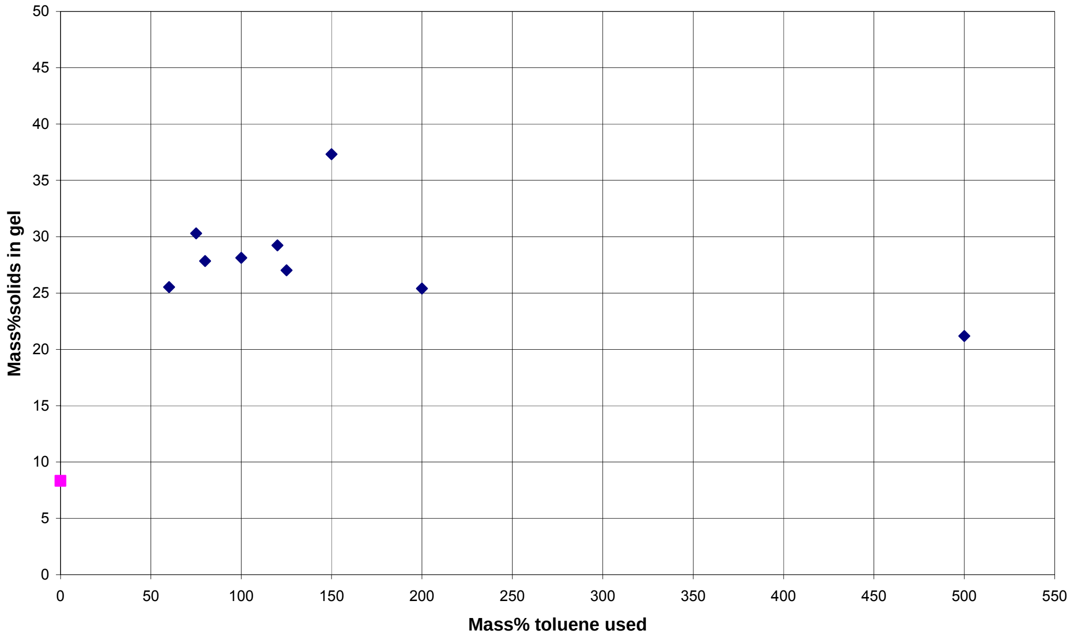


Figure 5.2.7: The effect of the amount of toluene added to clean gel on the removal of water from the gel (mass % solids in the gel)

The amount of toluene added (above 60 %) does not seem to have an influence on the removal of water. The mass solids in the gel lie in the range of 30 %. This cannot be compared with the results of Morifi (2002) because it is not clear how the results in this report were calculated.

5.2.7.2. Toluene added at the beginning of washing

Figure 5.2.8 shows the effect that the addition of toluene has on the removal of DMF from the RCG, using a water to RCS or RCG ratio of 0.6:1.0. From 0 % to 120 % toluene added, a difference of almost 20 % in the DMF removal can be seen. Therefore the addition of toluene does make a big difference in the removal of the DMF from the RCG. This is because the toluene is water-immiscible and pushes more water, together with DMF, out of the gel than normally. The more toluene used, the better the separation. A limit with regard to the amount of toluene should be found for optimum separation.

Figure 5.2.9 also shows the effect of toluene added, comparing the addition of 120% toluene with a normal wash, for water to RCS or RCG ratios of 0.2:1.0 to 0.6:1.0. It can be seen that in the second stage, with the 0.4:1.0 ratio of water to RCG, the removal of DMF is better by a difference of 27 %. Also, 27 wt % solids are achieved at the eighth wash with this ratio of water, which is very good.

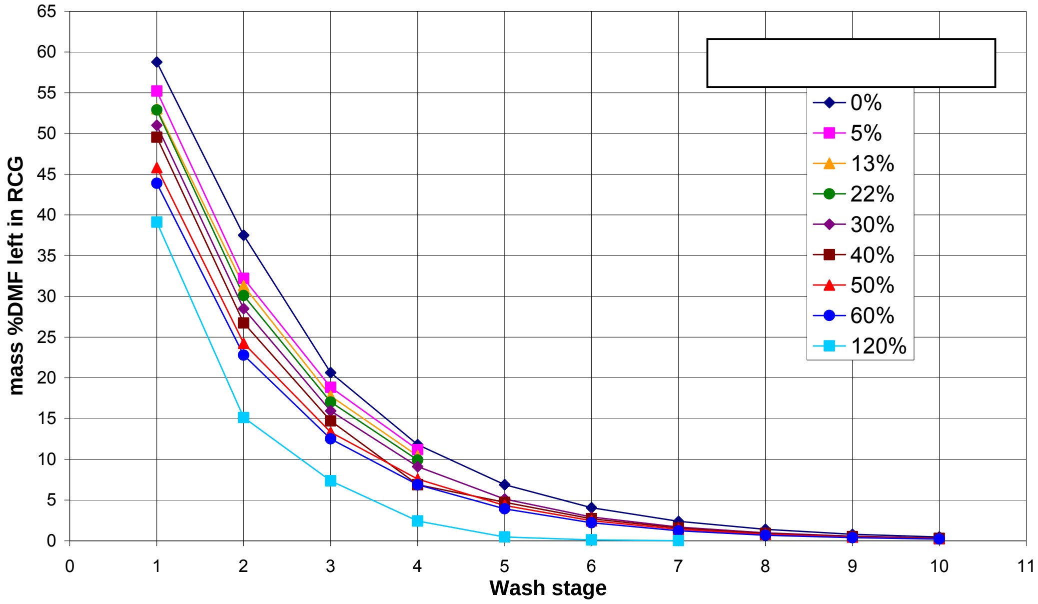


Figure 5.2.8: The effect of adding toluene to RCS at the beginning of washing, on the removal of DMF from RCG

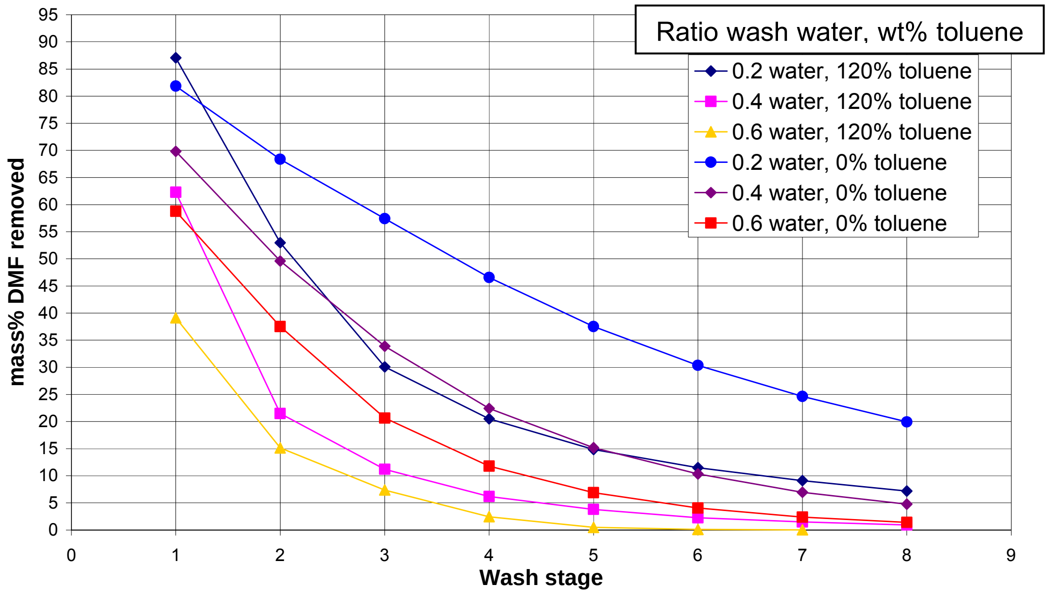


Figure 5.2.9: The effect of adding toluene to RCS at the beginning of washing, on the removal of DMF from RCG

5.2.8. The effect of using dimethylacetamide as solvent

Figure 5.2.10 shows the effect of using DMAC as organic solution compared with DMF on the washing. The first wash shows a higher amount for the DMAC, but the rest of the washes are almost the same. Therefore the use of DMAC as solvent would not contribute to more efficient separation of the solvent from the Refcoal.

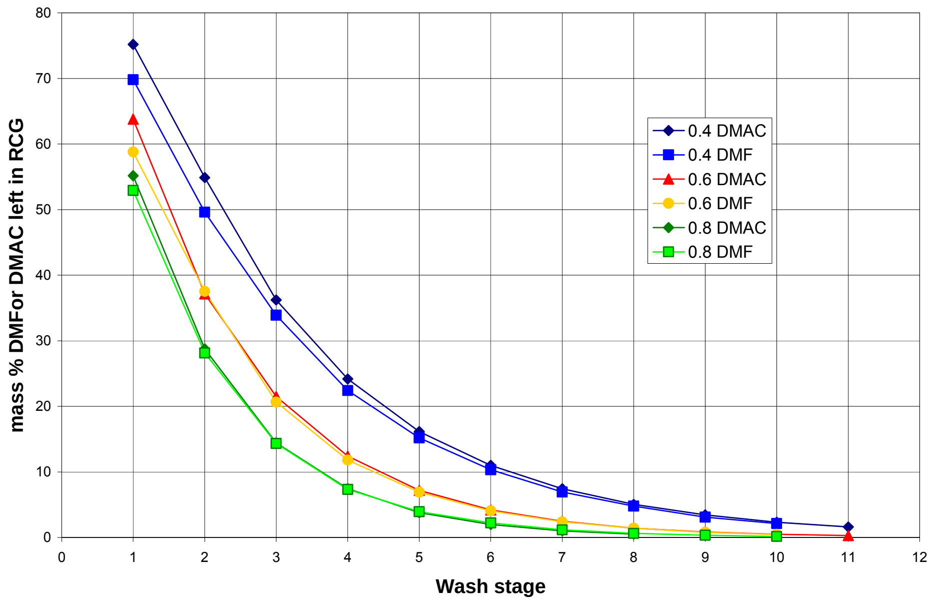


Figure 5.2.10: The effect of using a different organic solution, on the washing of the RCG

5.3. Separation by Filtration

5.3.1. The effect of the amount of wash water used

The experiment using a water to RCS ratio of 0.2:1.0 could not be completed due to the poor fluidity of the mixture after the addition of the first wash water. Using a ratio of 0.4:1.0, only two washes could be completed. This was due to the loss of material during transfer from mixing to filtration. However, comparing these results with those of the ratio of 0.6:1.0, as expected, better removal of DMF was achieved with more water.

5.3.2. The effect of gel agglomeration

Figure 5.3.1 shows the effect that toluene has on the pressure filtration method of separating DMF from the RCG. Only the addition of 120 % toluene effects a significant improvement in the separation. This could be due to the high pressures applied to the RCG – the filtrate could be pushed out of the cake to a certain extent, whether or not toluene was added.

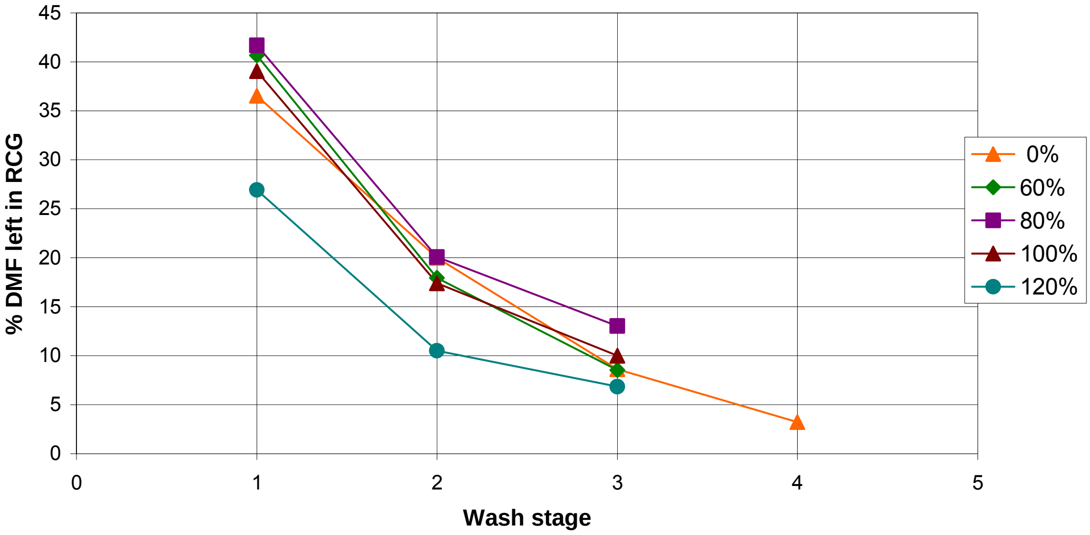


Figure 5.3.1: The effect of toluene on the separation of DMF from RCG

Although the addition of toluene from 60 % to 100 % did not have a significant effect on the separation of DMF from the RCG using pressure filtration, the breakthrough times decreased, compared with no toluene added. This is probably because the toluene breaks down the RCG and forms a less-dense medium which allows the gas to pass through more easily. The addition of 120 % toluene made almost 10 % difference in the first stage. The percentage solids in the RCG after stage three, using 120 % toluene, is approximately 28 %, whereas at the same stage, for 0 % addition of toluene the solids percentage is only 12 %. This implies that the DMF can be removed more efficiently when toluene is used with the filtration process.

5.4. Comparison of Centrifugation and Filtration Experiments

Figure 5.4.1 compares the use of centrifugation and filtration as separation techniques. It can be clearly seen that using pressure filtration gives better results – up to 20 % better recovery of the DMF. Pressure filtration can apply more driving force than the centrifuging forces. Approximately the same masses of raw materials were used and the pressure filtration results were achieved in a shorter time period. For example, the normal centrifuging time was 20 min per stage and the pressure filtration did not take longer than 5 min, for breakthrough to occur, per stage.

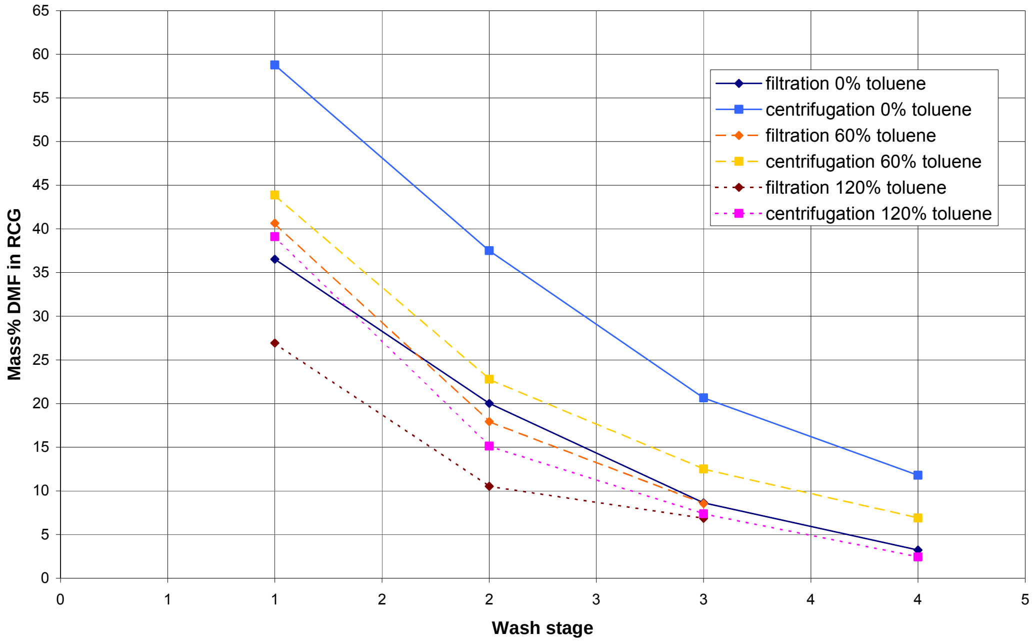


Figure 5.4.1: Mass % of DMF removed per stage; comparison of the use of centrifugation and filtration as separation techniques

5.5. Counter-Current Washing

5.5.1. Water to Refcoal solution ratio of 0.8:1.0

Only six stages were used to obtain a final DMF concentration of 1% (mass) in the final RCG_6. This was done under the assumption that the calculation of the number of stages was too conservative and to shorten the experimental time. But, as can be seen in Table 5.5.1, the DMF in RCG_6 is still too high at 9 %. Table 5.5.1 gives the data for the streams in each stage on the basis of 25 g RCS_0.

Table 5.5.1: Stream information on the counter-current washing experiment using a water to RCS ratio of 0.8:1.0

	Total (g)	Fraction DMF	Fraction Water	Fraction Solids		Total (g)	Fraction DMF	Fraction Water
RCS_0	25.00	0.92	0.00	0.08	**S_1**	23.19	0.75	0.25
RCG_1	24.33	0.62	0.30	0.08	**S_2**	22.53	0.47	0.53
RCG_2	24.63	0.41	0.50	0.08	**S_3**	22.83	0.29	0.71
RCG_3	23.50	0.28	0.64	0.09	**S_4**	21.69	0.17	0.83
RCG_4	22.61	0.20	0.71	0.09	**S_5**	20.80	0.12	0.88
RCG_5	22.03	0.15	0.76	0.09	**S_6**	20.22	0.07	0.93
RCG_6	21.81	0.09	0.82	0.09	**S_7**	20.00	0.00	1.00

5.5.2. Water to Refcoal solution ratios of 0.6 and 0.4:1.0

The final experiments done with these water to RCS ratios were unsuccessful. The water-DMF solution (S_2) added to the RCS_0 did not gel the RCS_0, and therefore no separation could take place during centrifuging. This was probably due to the high concentration of DMF in the solution (S_2).

Further investigation into the gelling of the RCS has been done and is discussed in Section 5.5.3.

5.5.3. Gelling tests

No significant relationship was observed between the ratios of solids to water to DMF, and the formation of the gel. Separation of the DMF from the Refcoal is dependent on the formation of a gel and the expulsion of a supernatant. This does not occur if not enough water is present. When only water is added and not a solution of water and DMF, the limit of gelling is at a water to RCS ratio of 0.07:1.0. However, with this ratio no separation occurs with centrifugation.

It was also observed that if the RCS was diluted too much with DMF, it was difficult to achieve precipitation and separation with the addition of water.

Chapter 6. CONCLUSIONS AND RECOMMENDATIONS

6.1. Separation by Centrifugation

6.1.1. The effect of the amount of wash water used

Using more water during the washing stages gives a higher removal of DMF, as can be expected. However, this will lead to a high running cost due to the later stage of separation of the DMF from the water. The DMF has to be recycled back into the process with the minimum amount of water.

One would like to use as little water as possible, but this pushes up the number of stages, which in turn pushes up the manufacturing costs. An optimum amount of water cannot be decided on the basis of only this information.

The solids concentration increases with each stage of washing, but when water to RCS ratios of 0.8, 1.0 and 1.2 to 1.0 are used, from stage 9 the densities decrease. This is probably due to mixing inefficiency, causing air-entrainment of coal particles, which decrease the density, thereby making them float.

The effect of the stirring efficiency on the occurence of air-entrainment, and its influence on the gel densities, should be evaluated. More effective mixing should be considered. The use of baffles during mixing will decrease the air-entrainment.

6.1.2. The effect of stirring and centrifugation time

The stirring time also has an effect on the density of the gel. It is thought that if the mixture is stirred too long, too much air is entrained in the gel, lowering its density. As mentioned in section 6.1.1, mixing efficiencies should be investigated.

The centrifuging time also has an effect on the density of the gel, but the limit seems to be at 20–25 min. This is because the gel reaches a maximum density and further applied force will not increase it.

6.1.3. The effect of wash water temperature

If water at 0°C is used in normal washing, it can improve the removal of the DMF by 5 %. This is not very significant, and too much energy will be needed compared with the increase in efficiency gained.

6.1.4. The effect of syneresis

Syneresis has a positive effect on increasing the density of the RCG. It was possible to increase the solids percentage in the gel through syneresis from 12.5 wt % up to 20 wt %. This was with a water to RCS ratio of 0.6:1.0 and the addition of 120 % toluene.

Using heated standing tanks to expel the supernatant and thereby improve the gel density will decrease the number of washing stages needed, at a low cost.

Further investigation into syneresis is recommended. This is an inexpensive way of increasing the density of the gel, thereby improving the separation of DMF from RCG.

6.1.5. The effect of gel pH

Water with a lower pH did not influence the separation significantly. However, as mentioned in the literature, a lower pH will limit the removal of NaOH from the RCG (Manganyi, 2001). This means that the addition of an acid will not have a positive effect on the washing procedure, but the extent of the influence on the removal of NaOH is not known. Therefore, when HCL is used for the removal of impurities, the effect of the removal of NaOH should be looked at more closely.

6.1.6. The effect of gel agglomeration

6.1.6.1. The addition of toluene at the end of a wash

Up to 30 wt % solids in the RCG could be achieved with the addition of toluene to clean RCG. This was found with the addition of toluene at 60 % and higher. Lower amounts of toluene were not investigated. It would be possible to use lower amounts of toluene, but no significant improvement was found with the higher amount.

The stirring energy put into mixing the toluene with the RCG is very important – with gentle stirring, the efficiency was much lower.

6.1.6.2. The addition of toluene at the beginning of a wash

When toluene is added at the beginning of a wash, an improvement of up to 20 % on the percentage of DMF removed can be achieved, with the addition of 120 % toluene. A solids concentration of 27 wt % could be achieved with a water to RCS ratio of 0.4:1.0 and the addition of 120 % toluene. This is good compared with washes without toluene.

The use of toluene results in a high amount of toluene in the water-DMF solution, which then needs to be separated via distillation. A residue curve of water-DMF-toluene is shown the Appendix (Figure 8.1). This shows that there is no abnormal behaviour when toluene is present in the water-DMF composition. The only azeotrope is the one between water and toluene, as expected because they are insoluble. Toluene would therefore not have a negative effect on separation via distillation. Also, it is suspected that the concentration of toluene in the DMF will not have a big effect on the extent of the extraction of the coal because it is organic. This is good news if such high amounts of toluene were to be used. However, it is important to investigate the effect that toluene will have on the distillation of the water and DMF, as well as on the extraction process if it is recycled back with the DMF.

6.1.7. The effect of using dimethylacetamide as solvent

The use of DMAC as organic solution does not have an effect on the washing, but it could be a better choice than DMF due to it being less toxic. On experimental scale, the use of DMAC is more expensive. This could change when the Refcoal process is scaled up due to increase in demand. The outcome of this experiment shows that if DMAC is chosen, it will not affect the washing efficiency.

6.2. Comparison of Separation by Pressure Filtration and Centrifugation

6.2.1. The effect of the amount of wash water used

Pressure filtration, using pressures up to 600 kPa(g), produces a 20 % improvement of DMF removal over normal centrifuge washing. The time taken for pressure filtration is 5 min, in comparison with 20 min for centrifugation. The process therefore appears to be better overall. The costs were not compared and therefore no judgment can be made as to the economic aspects of the two processes.

6.2.2. The effect of gel agglomeration

The addition of 120 wt % toluene at the beginning of filtration gives a 10 wt % improvement in DMF removal, in the first stage of washing, compared with no toluene added. It also gives a very high solids percentage in the gel of 28 wt %, after three stages. With centrifugation, this could be achieved with the addition of 120 wt % of toluene at the eighth stage of washing.

Pressure filtration appears to be a better option than centrifuging, increasing the density of the gel and decreases the separation time. However, these experiments were done on a laboratory scale and scaling-up has proved problematic. The cost differences between centrifuging and pressure filtration should be investigated.

Filtration should be further investigated. Different wash water temperatures and other water to RCS ratios could be looked at. The cake could be washed without removing it and mixing it with water, thereby displacing the solution with water. More details, such as the type of filter medium, could also be investigated. Dickey (1961: 134-135) gives information on choosing a filter medium.

At the end of filtration, the cake could be dewatered as described by Hosten & San (2002). Gas could be sucked or blown through the cake to displace the retained water. This would decrease the evaporation energy needed to dry the Refcoal.

6.3. Counter-Current Washing

Using a water to RCS ratio of 0.8:1.0 in the counter-current experiments required seven stages and produced a water-DMF solution containing 75% DMF.

Experiments using water to RCS ratios of 0.4:1.0 and 0.6:1.0 could not be completed because the solution (S_2) added to the RCS did not contain enough water to gel the RCS and therefore no separation could take place.

The attempt to determine a pattern in the ratios of water to DMF to solids, in order to be able to gel and separate the RCS into RCG and a supernatant, was unsuccessful.

Counter-current washing compared favourably with single-stage washing on the basis of a water to RCS ratio of 0.8:1.0: single-stage washing required ten stages and about eight times more water compared with the seven stages of counter-current washing. Single-stage washing would therefore require eight times more water to be removed during distillation. Counter-current washing is the more effective method, although the gelling of the RCS would be a constraint on minimising water usage.

It is recommended that counter-current washing experiments using pressure filtration should be done.

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APPENDIX

Water-DMF-toluene residue curve

Figure 8.1 shows the residue curve of water-DMF-toluene. There is an azeotrope at the water-toluene interface – this is expected due to the insolubility of water in toluene.

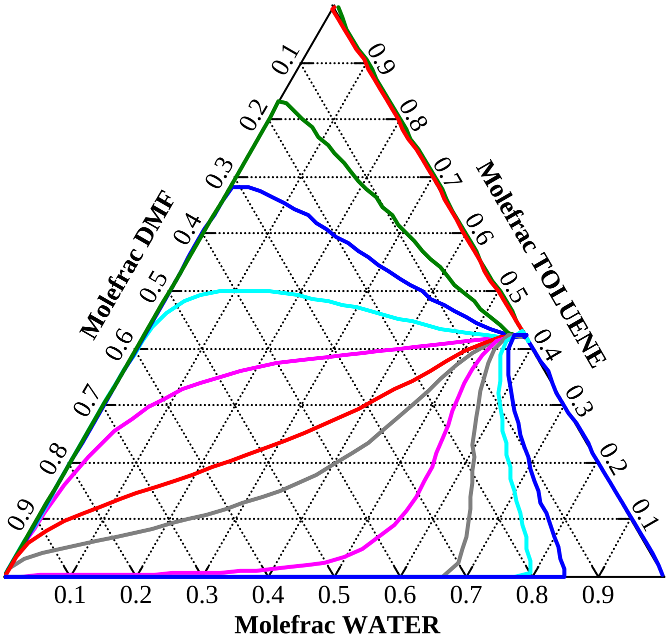

Figure 8.1: Residue curve of water-DMF-toluene