

Design and characterization of asymmetrical porous nickel membranes

Ruan Botha

BPharm

November 2006

*Dissertation submitted in partial fulfillment of the requirements for
the degree*

Magister Scientiae

in Pharmaceutical Chemistry

*at the North West University, Potchefstroom
Faculty of Health Sciences.*

Supervisor:

Prof H.M. Krieg

Assistant supervisor:

Prof J.C. Breytenbach

Assistant supervisor:

Dr G Lachmann

Design and characterization of asymmetrical porous nickel membranes

R Botha

Ek wil graag die volgende persone en instansies bedank:

- Die Hemelse Vader wat my die krag gegee het om hierdie studie te kon voltooi.
- My ouers, Theuns en Tonetti vir hulle deurgaanse ondersteuning en leiding, asook by broer Innes, sus Ane, asook die res van my familie.
- Aan Prof Henning Krieg, 'n besondere woord van dank, vir die leiding wat hy verskaf het op akademiese vlak, maar ook vir sy verfrissende mense-insig wat hy sonder verwyl met my gedeel het.
- Aan Prof Jaco Breytenbach, wie se aansteeklike inspirasie en entoesiasme om die studie te onderneem ek nie ligtelik kan opneem nie.
- Dr Gerhard Lachmann. Dit was eintlik sy idee om 'n nikkelmembraan te maak...
- Ek sou moeilik die studie kon voltooi het as dit nie was vir Hertzog Bissett nie. Sy behulpzaamheid en idees kom uit in al die fasette van die studie.
- My 'office mates', Marissa Alves en Dewald Kapp vir eindelose pret asook my mede nagraadse studente by Chemie, Chemiese Ingenieurswese en Farmaseutiese Chemie.
- Al die lede van die Potchefstroomse Universiteitskoor en aan Awie van Wyk vir 6 jaar se onvergeetlikheid, asook die lede van Flip-a-Coin acapella sanggroep.
- Aan Jackie Coetser, Faan Cloete, Daleen Cloete, Ras en Annemie de Lange, Elsabe Retief, Fred en Antoinette Cloete en Theuns en Tonetti Botha vir finansiële ondersteuning.
- My vriende wat ek nou in Potchefstroom agterlaat.
- NRF en SST vir finansiële ondersteuning.

Ruan Botha
Potchefstroom
November 2006

Only individuals have a sense of responsibility.

– Friedrich Nietzsche

ABSTRACT

As an alternative to organic membranes, ceramic membranes are suitable for the chemical industry due to their intrinsic thermal, chemical and mechanical stability. The centrifugal dispositioning technique has the advantage that it produces membranes that are asymmetrical with a smooth inner surface. In this study, nickel powders were used in the place of regular α -alumina powders to produce an asymmetrical porous membrane, and to determine its characteristics.

Sub-micron nickel powders can be produced by the hydrothermal reduction of a nickel salt with hydrazine. The particles obtained are of the correct size and size distribution and can be processed to be suitable for centrifugal dispositioning. Dispersants like polyacrylamide-co-diallyldimethylammoniumchloride, polyvinylpyrrolidone (PVP) and ammonium-polymetacrylate (APMA) were investigated to determine their ability to stabilize Ni powder in an aqueous dispersion.

Nickel powder manufactured by the hydrothermal reduction of a nickel salt with hydrazine were moulded into a tubular membrane by means of the centrifugal dispositioning technique. A stable dispersion was made with PAAco with little agglomeration or segregation. The membranes were successfully removed from the stainless steel moulds without breakage of the membrane. The greencasted membranes obtained were sintered without membrane failure, where after they were subjected to numerous tests to determine their characteristics.

SEM photographs were taken from the inner surface and cross-sections to determine the morphology of the membranes. It was demonstrated that a change in the crystal phase occurred at 1200°C, changing the morphology as well as the membrane characteristics. The nickel membrane shrinkage during the sintering experiments was found to increase linearly. It was shown with mercury intrusion that the bimodal pore size distribution of the membranes decreased with increasing sintering temperature, while larger pores were exchanged for smaller pores. It was found that water permeation varied from 5 to 69 L.m⁻².h⁻¹.bar⁻¹, depending on the sintering temperature (950°C to 1250°C) of the membrane. The water permeation decreased linearly with increasing sintering temperature.

OPSOMMING

As alternatief vir organiese membrane kan keramiekmembrane gebruik word omrede hulle goeie termiese, chemiese en meganiese eienskappe. Die sentrifugale dispositioneerings tegniek kan ingespan word om membrane te vervaardig wat asimmetries is en oor 'n gladde binneoppervlakte beskik. In hierdie studie is nikkel poeiers gebruik in die plek van α -alumina poeiers om asimmetriese membrane te vervaardig d.m.v. sentrifugale dispositioneering en om hulle karakteristieke eienskappe te bepaal.

Sub-mikron nikkel poeier kan vervaardig word d.m.v. 'n hidrotermiese reduksie van 'n nikkelsout met hidrasien. Die partikels wat gepresipiteer word is die korrekte grootte en grootte distribusie, en kan geprosesseer word om geskik te wees vir die sentrifugale dispositioneerings prosedure. Dispergante soos poliakrielamied-co-diallieldimetielammoniumchloried (PAAco), polivinilpirolidoon (PVP) en ammonium-polimetakrilaat (APMA) was ondersoek om hulle dispergerings vermoë te bepaal in waterige media.

Die nikkel poeiers vervaardig met hidrotermiese reduksie kon suksesvol in 'n tubulêre membraan gevorm word d.m.v. die sentrifugale dispositioneerings tegniek. 'n Stabiele dispersie van nikkel partikels en PAAco kon geformuleer word met min gepaardgaande segregasie en agglomerasie. Die membrane kon verwyder word uit die vlekrye staal patroon (waarin dit gevorm was) sonder dat die membraan kraak of breek. Hierna is dit gesinter in 'n program sonder dat die membrane gebreek het, waarna dit geonderwerp was aan verskeie karakteriseerings eksperimente.

SEM foto's was geneem om die morfologie van die nikkel membrane te bekyk. Dit was opgemerk dat die nikkeloksied membraan 'n kristalfase verandering ondergaan het by temperature hoër as 1200°C wat die eienskappe en karakteristieke van die membraan gealter het. Die krimpings van die membrane was lineêr tydens sintering. Daar was gevind met kwik intrusie dat 'n bimodale poriegrootte verspreiding verdwyn het namate die sinteringstemperatuur verhoog het, met groter porieë wat verruil word vir kleiner porieë. Die water permeasie het gevarieer van 5 tot $69 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$ afhangende van die sinterings temperatuur (950°C tot 1250°C) en het lineêr afgeneem met verhoogde sinterings temperatuur.

CONTENTS

ACKNOWLEDGEMENTS.....	..ii
------------------------------	-------------

ABSTRACT.....	..iv
----------------------	-------------

OPSOMMING.....	..v
-----------------------	------------

CONTENTS.....	..vi
----------------------	-------------

Chapter I: Introduction	1
--------------------------------------	----------

1.1. Introduction	2
-------------------------	---

1.2 Aims and objectives of the dissertation.....	3
--	---

1.3. Structure of the dissertation	4
--	---

1.4. References.....	5
----------------------	---

Chapter II: Literature review.....	6
---	----------

2.1. Introduction	7
-------------------------	---

Contents

2.1.1. Basic membrane principles	8
2.2. Powder manufacturing	10
2.3. Dispersion formulation	13
2.4. Centrifugal dispositioning	16
2.5. Sintering	17
2.6. Membrane characterization	19
2.6.1. Permeability	19
2.6.2. Membrane strength	20
2.6.3. Mercury porosimetry	20
2.6.4. Membrane surface	21
2.7 Conclusions	22
2.8 References.....	23

Chapter III: Experimental..... 28

3.1. Nickel powder manufacture	29
3.1.1. Hydrothermal reduction procedure	29
3.1.2. Powder purification and preparation for dispersion formulation	31
3.2. Powder characterization	31
3.2.1. Particle size analysis.....	31
3.2.2. EDS analysis.....	32
3.2.3. XRD analysis.....	32
3.3. Dispersion formulation	32
3.3.1. Dispersion stability	33
3.3.2. Dispersion formulation for membrane manufacture	33
3.4. Centrifugal casting	34
3.5. Sintering	35

Contents

3.6. Membrane Characterization.....	36
3.6.1. Dimensions and shrinkage.....	36
3.6.2. Mercury porosimetry	36
3.6.3. Water permeability	36
3.6.4. SEM	38
3.6.5. Membrane strength.....	38
3.7. References.....	41

Chapter IV: Results and discussion..... 42

4.1. Introduction	43
4.2. Nickel powder manufacture	43
4.2.1. Nickel precipitation reaction.....	43
4.2.2. Influence of EtOH concentration.....	46
4.2.3. Nickel powder purification.....	48
4.2.4. Nickel powder agglomeration	49
4.2.5. Powder characterization	50
4.2.5.1. Particle size.....	50
4.2.5.2. XRD and EDS	52
4.3. Dispersion formulation	53
4.4. Centrifugal dispositioning.....	59
4.5. Sintering.....	62
4.6. Membrane Characterization.....	63
4.6.1. Dimensions and Shrinkage.....	63
4.6.2. SEM	66
4.6.3. Mercury porosimetry	69
4.6.4. Membrane Strength.....	73

Contents

4.6.5. Water permeance	74
4.7. Conclusions	79
4.8. References.....	81

Chapter V: Final conclusion and recommendations 84

5.1. General overview	85
5.2. Conclusions	86
5.3. Recommendations	86
5.4. References.....	87

Chapter I

General Introduction

1.1. Introduction

The importance of separation processes for the chemical industry is well known, and the applications for membrane processes in this field have grown significantly, branching out to various parts of industry. A membrane can be described as a perm selective barrier between two phases. Membranes can mainly be divided into polymeric and inorganic membranes, the latter of which will be the focus to this study. Both membrane types have advantages and disadvantages, but for applications specifically in the chemical industry, polymeric membranes are often deemed unfit. For these harsh environments, inorganic membranes could rise to the occasion because they are both physically and chemically stronger which means that they can endure harsh chemical environments as well as high temperatures and pressures. Apart from the stability there are however three more equally important requirements that a membrane should meet before it might become suitable for a commercial application. This includes selectivity, permeance and stability.¹

While inorganic membranes can be manufactured by a number of ways, the focus in this study will be on centrifugal dispositioning. Centrifugal dispositioning produces tubular membranes that have unique properties because they are asymmetrical. This entails the production of a membrane with a pore size gradient in a single experimental procedure with the denser side on the inside of the tube and the more porous side on the outside. The porosity of the latter support structure enables the membrane to have increased permeance, but the biggest advantage on these membranes is a smooth inner surface.² The materials used to produce this membrane are paramount because it will determine the final characteristics of the membrane. Ceramic membranes manufactured by centrifugal dispositioning proved to be brittle and have a high manufacturing cost.³ Alternatively, membranes may be manufactured using other materials which might address these shortcomings. Many authors including Biesheuvel *et al* , Steenkamp *et al* ⁴, Bissett ⁵ and Zah *et al* ⁶ have produced porous α -alumina membranes by means of centrifugal dispositioning technique. In this study the focus will be on producing a porous nickel membrane by the same manufacturing procedure and comparing its properties to its α -alumina counterparts. Powder dispersivity, membrane formation and sinterability of a nickel membrane will also be investigated.

1.2. Aims and objectives

The aim of this research is to manufacture and characterize a porous nickel membrane by means of the centrifugal disposition technique. This will be achieved by means of the following experimental procedures:

- Manufacture a nickel powder that is chemically pure, which has the necessary properties needed for the manufacture procedure which include:
- Formulate a stable dispersion of the nickel particles.
- Produce a membrane from the latter dispersion by means of the centrifugal dispositioning technique.
- Development of a sintering programme producing optimal membranes.

Generally the objectives of the project are to:

- Produce a nickel membrane of which the characteristics are comparable to the α -alumina membranes.
- Reduce the manufacturing cost.
- Improve permeance.

1.3. Structure of the dissertation

The theory on the manufacture of a porous nickel membrane by means of centrifugal dispositioning technique is discussed under the topics centrifugal casting, sintering and membrane characterization in Chapter II. The required procedure towards the manufacture of the nickel

powders and the potential dispersants for formulating the powder into a stable dispersion is also discussed in this section.

Chapter III entails the experimental procedure followed to produce the nickel membranes while Chapter IV contains the results and discussions. The layout of Chapters III and IV is given in Figure 1.1.

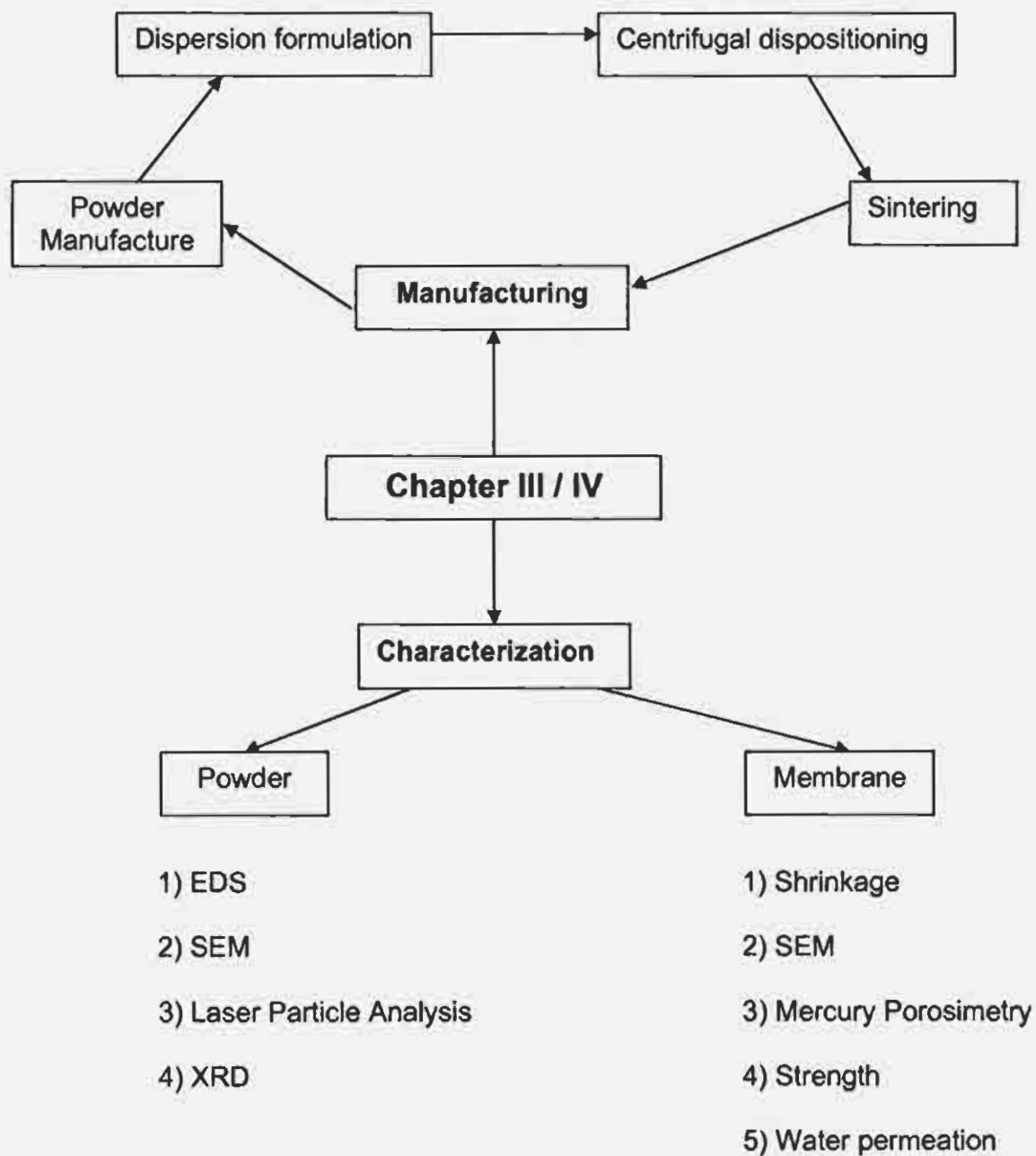


Figure 1.1. Layout of Chapters III and IV

1.4. References

- ¹ M.Mulder, Basic principles of membrane technology, 2nd edition, Kluwer Academic Press, 1996, Chapter 1, Introduction, p 7
- ² P.M.Biesheuvel, V.Breedveld, A.P.Higler, H.Verweij, Graded membrane supports produced by centrifugal casting of a slightly polydisperse suspension, *Chemical and Engineering Science*, **56(11)**, 2001, 3517
- ³ P.M. Biesheuvel, H. Verweij, Design of ceramic membrane supports: permeability, tensile strength and stress, *Journal of Membrane Science*, **156**, 1999, 141
- ⁴ G.C.Steenkamp, H.W.J.P.Neomagus, H.M.Krieg, K.Keizer, Centrifugal casting of ceramic membrane tubes and coating with chitosan, *Journal of Membrane Science*, **199**, 2002, 69
- ⁵ H.Bissett, Manufacture and optimization of tubular ceramic membrane supports, M.Sc dissertation, North West University Potchefstroom, 2005, South Africa, Chapter 3, Ceramic support optimization, p 33, 34
- ⁶ J.Zah, H.M.Krieg, J.C.Breytenbach, Pervaporation and related properties of time-dependent growth layers of zeolite NaA on structured ceramic supports, *Journal of Membrane Science*, **284**, 2006, 276

Chapter II

Literature Review

2.1 Introduction

There are basically two types of membranes, polymeric membranes and inorganic membranes, each with their own advantages and disadvantages. The focus of this work will be on inorganic membranes, since separation processes for the chemical industry require membranes that can endure high temperatures and are resilient to harsh chemical environments with high membrane strength.¹ It has been shown that inorganic membranes meet the above mentioned requirements.² While numerous authors have dealt with alumina based ceramic materials, this study will focus on a novel nickel based membrane. The manufacture of centrifugally dispositioned ceramic membranes has received significant attention in the last decade.^{3, 4} Composite membranes provide the mechanical strength (support) combined with a defect free top-layer, for example a zeolite providing the selectivity. The top-layer (e.g. zeolite) possesses its own chemical properties and pore sizes chosen to ensure that the required separation is attained.⁵ Nickel membranes have certain advantages and disadvantages when compared to alumina membranes. The advantages include that the use of nickel results in a cheaper membrane. A disadvantage of nickel is that it forms nickel oxide under high temperatures in leading to membranes that have a decreased strength. Alumina powder manufacture on the other hand is an extensive procedure that is time consuming and requires materials and apparatus that are expensive. The nickel powder used in this research is easy to produce, and can be made with simple equipment in a normal laboratory. The manufacture procedure is fast and easy. Finally of all the elementary metals, nickel is comparatively inert, and is not easily oxidized.⁶ An outlay of the literature is summarized in Figure 2.1

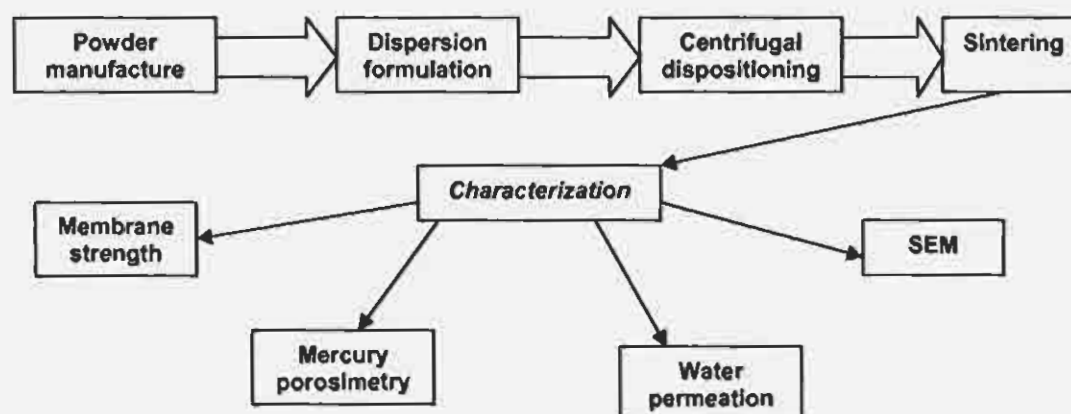


Figure 2.1. Literature summary

2.1.1. Basic membrane principles

As separation costs in industry rise, the focus is shifting more to finding alternative methods for separation. One of these alternative methods is membrane technology, which is likely to play an increasingly important role in reducing costs, and simultaneously reducing the negative impact on the environment.⁷ Membranes can be used for fractionation and purification, reaction mediation and concentration, and according to recent trends, membranes are being used increasingly in petrochemistry, environmental chemistry and as a mediator for new energy sources. A membrane can be defined as a selective permeable barrier between two phases. Certain components in a mixture will pass through the membrane (permeate), while others will be retained (retentate). This can be due to the physical and/or chemical properties of the components encountering the membrane. In Figure 2.2 a simple membrane process is illustrated.

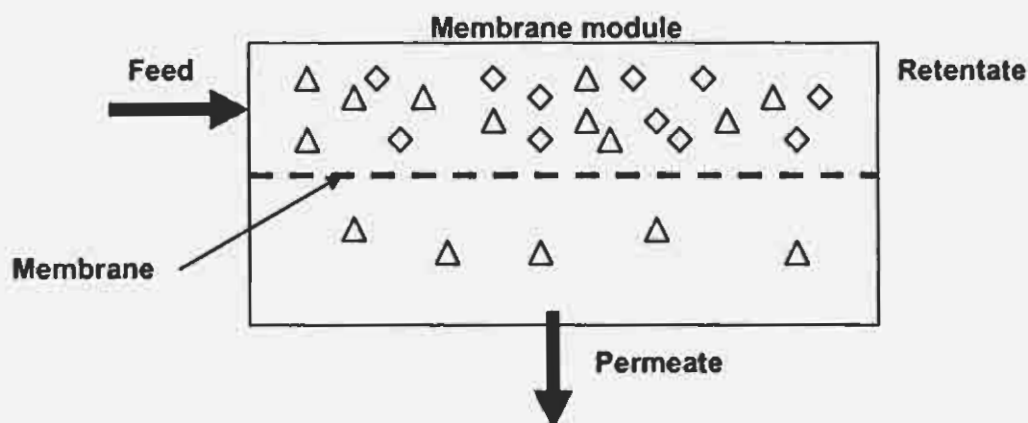


Figure 2.2 Illustration of selective membrane action

It is important that membranes have adequate flux and selectivity. Normally for any membrane a compromise has to be sought between flux and selectivity because an increase in flux will usually result in a decrease in selectivity and vice versa. The selectivity of the membrane will depend on the consistency of the pores, its size distribution and the absence of membrane defects. Flux on the other hand is directly related to porosity, size of the pores and the membrane thickness.

To express the selectivity of any membrane, the following two parameters are traditionally used:

- Rejection (R)
- Separation factor (α)

In terms of Figure 2.2, the rejection factor (R) can be calculated as follows:

$$R = \frac{C_i - C_p}{C_i} = 1 - \frac{C_p}{C_i} \quad (2.1)$$

where C_i equals the concentration in the retentate (in ppm) and C_p the concentration in the permeate (in ppm).

The separation factor (α) can be expressed as:

$$\alpha = \frac{\left(\frac{y_a}{y_b} \right)}{\left(\frac{x_a}{x_b} \right)} \quad (2.2)$$

where y_a and y_b are the concentrations of components A and B in the permeate, while x_a and x_b equal the concentrations of components A and B in the retentate.

Inorganic membranes, when compared to organic membranes possess increased thermal, chemical and mechanical stability. Inorganic membranes are also more resilient in terms of structural ability, swelling and compaction.⁸

For most applications where inorganic membranes are used, multiple layer membranes, i.e. composite membranes are used. The thin defect free top section is called the top-layer, which in

turn is reinforced by a supporting structure, which provides the mechanical strength. The top-layer is responsible for the separation. Both the top-layers and the support have to be able to endure elevated temperatures and harsh solvents for an extensive period of time in order for them to be commercially viable.^{2,9}

While most of the literature on inorganic membranes deals with the manufacture of α -alumina ceramic membranes, the same can however not be said for nickel membranes. Several authors have managed to manufacture nickel powders into a disk shaped membrane by pressing the powder into a green cast with a large industrial press. The powders were usually obtained from commercial suppliers in the form of nano-sized nickel powders. Authors who worked on the pressing of nickel powders into porous nickel membranes include Kim *et al*¹⁰ and Ryi *et al*¹¹

2.2 Powder manufacturing

Little is known on the manufacture of ultrafine nickel particles. Degen and Macek¹² were one of the first to publish work on the preparation of ultrafine nickel particles by means of hydrothermal reduction. This process entails the reaction of a nickel salt with a strong reducing agent for example hydrazine.¹³ Both these chemicals (nickel salt and hydrazine) are inexpensive and easy to obtain. The preparation of nickel particles by means of this method is, when compared to other production methods of ultrafine nickel particles, cost effective, and produces powders that can be cleaned easily in a polar environment. Other methods of producing fine nickel particles include the polyol method. This method is widely used and employs ethyleneglycol as a reducing agent at pH > 11. Other preparation procedures include the sonochemical decomposition technique and the irradiation technique. The nickel particles prepared by these methods are usually smaller than 1 μ m.¹⁴

Chemically, most nickel salts can be reduced by hydrazine under the correct conditions. According to Bettahar *et al*¹⁵ free Ni^{2+} ions are reduced to solid nickel precipitates according to the following simplified reaction equation:



In solution, water soluble nickel salts, for example nickel chloride, acetate, or nitrate will dissociate from the salt anion producing the Ni^{2+} cation. The subsequent reaction of Ni^{2+} with hydrazine (N_2H_4) involves the formation of a complex of nickel and hydrazine (Figure 2.2). These complexes usually occur in the form of bis(hydrazine)-Ni(II) chloride ($\text{Ni}(\text{N}_2\text{H}_4)_2\text{Cl}_2$) and tris(hydrazine)-Ni(II) chloride ($\text{Ni}(\text{N}_2\text{H}_4)_3\text{Cl}_2$) which in turn is converted to $\text{Ni}(\text{OH})_2$ in the nickel particle synthesis. After these nickel complexes have been formed, the addition of NaOH to the complex solution will liberate hydrazine from the nickel complexes. In the presence of NaOH, $\text{Ni}(\text{OH})_2$ is formed, which in turn is reduced to solid nickel by the liberated hydrazine.¹⁶ It is therefore clear that a basic (NaOH) environment is required for the hydrazine facilitated reduction of NiCl_2

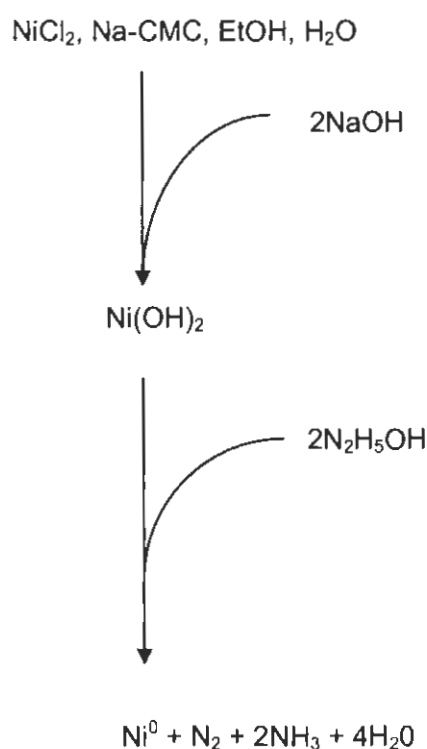


Figure 2.3. Schematic representation of nickel particle formation from nickel hydrazine complexes

To prevent the formation of inter-particle nucleation (agglomeration) during particle formation, various polymeric antiflocculants¹⁷ have been studied. It has been shown that an antiflocculant was usually sufficient in preventing this agglomeration (in a polar reducing environment).¹² The

polymers most commonly used include polyacrylamide (PAA) and polyvinylpyrrolidone (PVP) polymers.¹⁸ Park *et al*¹⁹ used sodium carboxymethylcellulose (Na-CMC) to prevent agglomeration. The Na-CMC's viscosity is pH sensitive and increases when the pH of the system is increased, thereby activating the polymer side chains, initiating steric polymer stabilization and at the same time providing OH⁻ groups necessary for production of Ni(OH)₂.^{20, 21}

Several other aspects will also influence the morphology of the nickel particles. Among these are the reaction temperature, nickel and hydrazine concentrations, and the antiflocculant concentration.²² The nickel particles produced in most cases had a spherical shape, and with mean particle sizes ranging from 0.35µm to 1.9µm. Typical variations observed due to concentration and temperature fluctuations are given in Table 2.1.

Table 2.1. Changes in particle size under varying reaction conditions.¹⁴

Increase of variable	Effect on particle size
[Hydrazine]	Decrease
[EtOH]	Decrease
Reaction temperature	Decrease
[Ni ²⁺]	Decrease
[Antiflocculant]	Decrease

To characterize nickel powders, analytic techniques like SEM and XRD are used to measure the size of the particles and to confirm the formation of nickel metal or oxide. While some authors have conducted the preparation experiment in non-aqueous (non-polar) systems, others have focused their attention on the preparation of the nickel particles in an aqueous (polar) system. Degen and Macek experimented with polar and non-polar systems, making use of di/triethylenamine and ethylene glycol (polar systems) as well as paraffin oil (non-polar system) as solvents. The advantage of some (ethyleneglycol, di/triethanolamine) of the non-polar systems includes the provision of a basic environment necessary for the precipitation and increased boiling temperature of the non-polar system leading to accelerated reaction rates. The main disadvantage of the non-polar systems includes the difficulty removing the system from the nickel particles after the precipitation reaction.^{12, 14, 19}

2.3. Dispersion formulation

The membranes produced in this study were made by dispersion processing. This process leads to membranes that have superior properties because ²³:

- Particles can be effectively dispersed in a liquid phase.
- Particles are mixed homogeneously.
- The centrifugal dispositioning that follows after dispersion formulation produces membranes that are uniform, defect free, and with smooth inner surfaces.
- Membrane failure during drying and sintering can be minimized because of the low amounts of organic additives used.

Disadvantages include:

- Cost.
- Increased processing time.
- Gravitational segregation.
- The dispersion manufacture requires technical competence.

For the centrifugal dispositioning process to be successful, the quality of the formulated dispersion is critical. Formulating a dispersion that is too stable will result in water and dispersant being retained in the sediment causing rapid redispersion after centrifugation of the particles initially deposited. If it is unstable, the particles that are dispersed will tend to flocculate which will give rise to inhomogeneous membranes with increased surface roughness.²⁴ According to Raming ²⁵ there are two mechanisms by which polymers stabilize particles in a dispersion namely:

- Steric stabilization
- Electrostatic stabilization

The differences between steric and electrostatic stabilization is that with steric stabilization the side chain groups of the polymer will repel the particles to which the polymer is attached from each other, while the existence of electrical charges will repel the particles from each other during electrostatic stabilization.²⁶

The polymers suggested for dispersion of nickel particles in the sub-micrometer size range, all employ steric stabilization of disperse the nickel particles. Steric stabilization of slurries is advantageous because of the following reasons:²⁷

- Steric mechanisms are effective in both aqueous and non-aqueous environments.
- Stabilization is equally effective at high and low solids loading.
- Flocculation is reversible.

It has to be kept in mind that the specific gravity (SG) of the nickel particles is more than twice that of the alumina particles.^{6, 27, 28} It has been suggested by several authors including Huyn *et al*²⁷ and Chou and Huang¹⁸ that the most appropriate polymers to disperse the sub-micron high gravity nickel powders are polyacrylamide (PAA), polyvinylpyrrolidone (PVP) and sodiummethacrylate (PMAA). According to the latter authors, PAA is superior when compared to any other polymer.^{18, 27} Huyn *et al*²⁷ specifically investigated the suitability of these polymers for dispersion of nickel particles that have been prepared by hydrothermal reduction of a nickel salt.

The stability of the polymers PAA, PVP, and PMAA has been expressed in terms of adsorption isotherm diagrams has been described. The stability of a certain polymer can be quantified by the amount of the polymer adsorbed to the particles at a certain concentration. The initial slope of the Langmuir isotherm is an indication of the adsorption affinity of the polymer for the particles, and can be used to predict the stability of the specific polymer-particle stabilization.²⁷ Figure 2.4 illustrates the adsorption isotherms of PAA, PVP and PMAA on Ni. From Figure 2.4. it can be assumed that the stability of the polymers confers to PAA>PVP>PMAA.²⁷

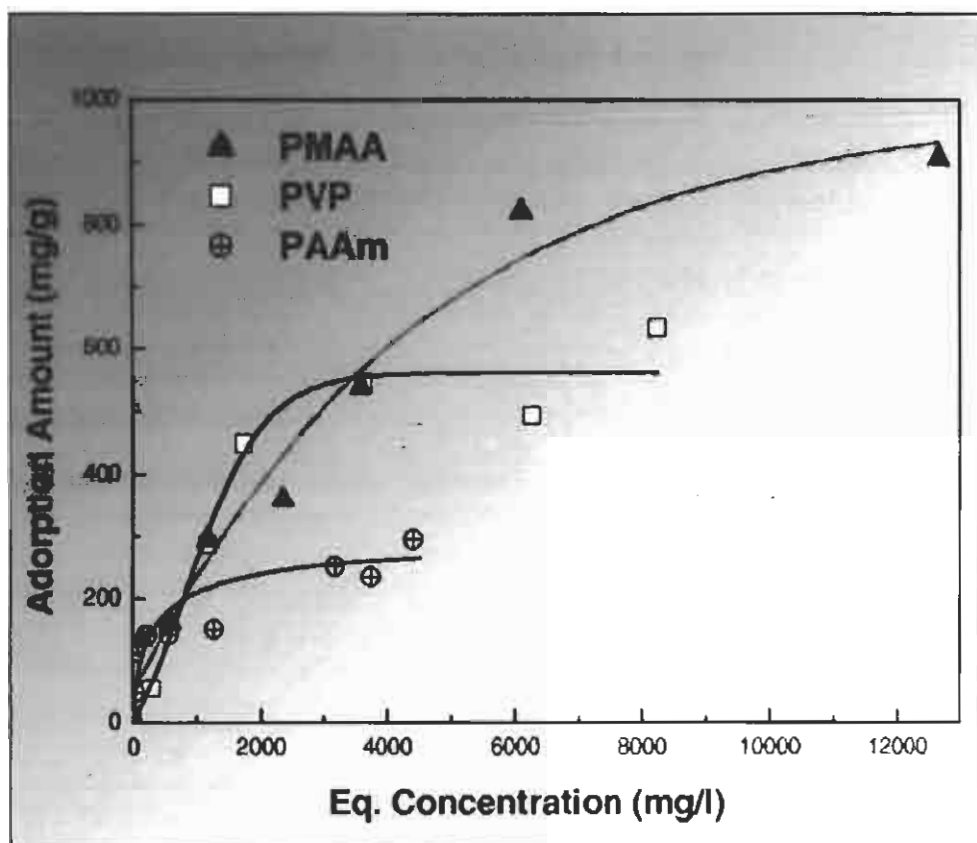


Figure 2.4. Adsorption isotherm of PAA, PVP and APMA ²⁷

Dispersion stability has also been quantified by means of optical methods. This method is similar to the turbidity method and employs a UV-vis spectrophotometer to measure the transmittance of a certain wavelength through a sample. As the dispersion breaks, the amount of light that passes through the sample cell is detected, and plotted as a function of time.

2.4. Centrifugal Dispositioning

The centrifugal dispositioning of ceramic powders is a process initially developed in the Netherlands by Verweij and Biesheuvel.²⁹ During centrifugal dispositioning the mass transfer of a dispersed nano-powder is attained by means of centrifugal forces. The powder is dispersed in a liquid phase with the aid of a stabilizer. As described in the dispersion Section 2.3, the dispersed powder is spun around its axis in a cylindrical mould for a specified period of time. While the powder is spun around its axis, the particles of the powder are forced to the sides of the mould at different rates. The larger particles which have a higher mass, will move to the side faster than the smaller (lighter) particles due to the difference in centripetal force. When the particles used for centrifugal dispositioning have a narrow size distribution and are not agglomerated, the formation of a close packed compact is obtained with the smallest particles on the inside and the largest particles on the outside (Figure 2.5).³⁰

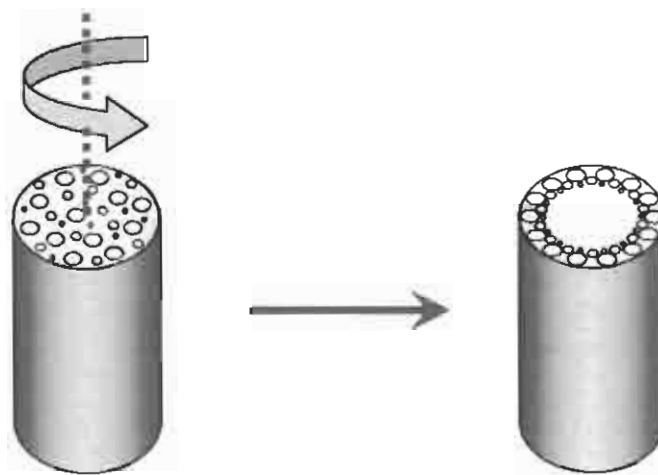


Figure 2.5. Centrifugal dispositioning

The illustration in Figure 2.5 demonstrates the rearrangement of large and small particles. The initial dispersion must be properly formulated to avoid formation of irregular membranes.

2.5. Sintering

Sintering is the next step in the production of a inorganic porous membrane. The purpose of sintering is to increase the strength of the membrane in order for it to endure elevated pressures. However sintering is usually accompanied by a decrease in porosity and pore size which is not desirable due to the direct proportionality between porosity, pore size and flux. Some of the changes that occur during sintering include a change in the pore shape, a decrease in the surface area, a decrease in the porosity and an increase in the neck area and grain size. During the sintering process mass transport occur between the individual grains in the compact. This occurs according to different mechanisms and is dependent on the relation between the melting temperature of the material used, and the sintering temperature applied. The mechanisms that take place during sintering are shown in Figure 2.6.³¹

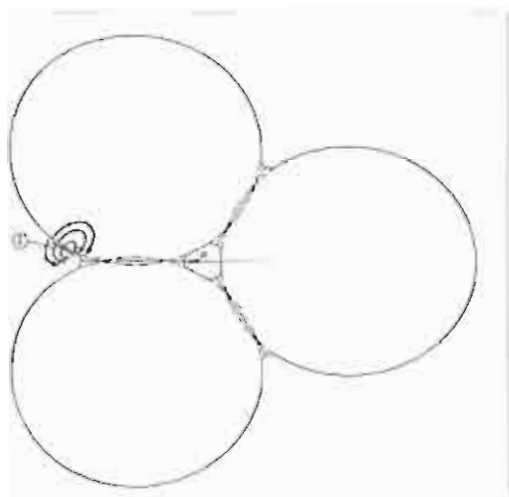


Figure 2.6. Mechanisms occurring during sintering

At lower sintering temperatures ($< 60\%$) surface diffusion (1) plays an important role.³² Particle joining and an increase in neck area between particles, and pore rounding occurs because of surface diffusion and surface smoothing, but this step does not bring about volume shrinkage. During this phase the strength of the membrane will increase, while the porosity will remain unchanged. This is ideal for a membrane support because of the high fluid permeance attained through the porous structure. When the sintering temperature increases, grain boundary diffusion

and diffusion through the lattice of the grains will produce both neck growth and volume shrinkage. In this case, membranes with a low permeance and high strength are obtained. While no work has been done on the sintering of porous nickel membranes prepared by centrifugal dispositioning, some authors have however discussed the physical changes that will take place during the sintering of nickel. Because of the nature of nickel at elevated temperature the metal will oxidize to nickel oxide (NiO) resulting in a change of colour from grey to green.³³ In mineralogy NiO is also termed bunsenite and takes on a crystal structure similar to that of NaCl (cubic).³⁴ The characteristics of nickel oxide under high temperatures have been discussed by Manene³⁵ and Bobrovskii *et al*³⁶ indicated that the crystal phase of nickel is extremely sensitive to impurities at temperatures above 1200°C. An increase in the thermal expansion coefficient was observed, including the presence of magnetic transformation.

2.6. Membrane Characterization

After the membrane has been manufactured, several characterization experiments can be carried out. As an asymmetrical porous nickel membrane has never been produced before, the characterization experiments will add new insight into the characteristics of a nickel membrane that has never before been described in literature.

2.6.1. Permeance

Characterization by means of water permeance is simple and therefore often used to characterize membranes. Furthermore it gives an immediate indication of the flux attainable with such a membrane. To measure the water permeance, a pressure difference is applied over the membrane, and the amount of water that permeates through the membrane is measured as a function of time. Subsequently, the water flow is obtained at various pressures. A graph of water flow as a function of pressure difference can then be plotted. By dividing the slope of the straight line of the latter graph by the surface area of the membrane, the water permeance is obtained. From this value, the membrane can be classified in terms of the type of membrane process applicable, i.e. micro, nano, or ultrafiltration.

Several factors will influence the permeance of a membrane such as the initial powder particle size, sintering temperature, and the amount of dispersant used to stabilize the dispersion. These effects can further be expressed in the Hagen-Poiseuille equation:

$$J = \frac{\varepsilon}{\tau} \frac{r^2}{8\eta} \frac{\Delta P}{\Delta x} \quad (2.3)$$

where J is the flux ($\text{L}\cdot\text{h}^{-1}\cdot\text{m}^2$) across the membrane at force $\Delta P/\Delta x$, where ΔP equals the pressure difference (N/m^2) and Δx the membrane thickness. ε equals the porosity, η the viscosity ($\text{Pa}\cdot\text{s}$), τ the tortuosity (2.5 for spherical particles), and r the mean pore radii (μm). The unit for permeance is $\text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$.³⁷

2.6.2. Membrane Strength

As membranes will be subjected to high pressures, it is important to investigate the strength of an inorganic membrane. The strength of the membrane will basically depend on the porosity and the size of the pores present. The formation of agglomerates prior to sintering will negatively affect the tensile strength.³⁸ Literature has offered several methods how the strength of membranes can be tested. These tests include the miniaturized disk bend test, when only small quantities of membrane are available,³⁹ the crack opening displacement measurement,⁴⁰ the single edge notched beam applied under 3 point loading,⁴¹ the compact tension method,⁴² the indentation technique,⁴³ and the scratch test.⁴⁴ According to the scratch test NiO is reported to have a Mohs hardness of 5.5⁴⁵ whereas it is 9 for alumina (diamond = 10)⁴⁶ Steenkamp *et al* and Zah *et al*⁴⁷ investigated the strength of ceramic centrifugally dispositioned membranes with a three point bending test, while a technique developed by Bissett was used in this study.

2.6.3. Mercury porosimetry

By means of non-wetting mercury intrusion porosimetry, structural information relating to pore size, pore size distribution and porosity can be obtained from a porous structure. The initial technique was proposed by Washburn in 1921 stating that by forcing mercury into a porous structure, the pore size distributions can be determined. The Washburn equation states that:

$$P = \frac{4\gamma \cos \theta}{d} \quad (2.4)$$

where γ equals the surface tension of mercury (0.48 N.m⁻¹), θ the contact angle between mercury and the material ($\approx 130^\circ$), d the pore diameter (m) and P the pressure applied on mercury (Pa). The volume of mercury that was forced into the pores can be used to estimate the pore size distribution. For mercury intrusion calculations the assumption is made that the pore geometry is cylindrical, and hence larger pores that are only accessible through smaller pores will be incorrectly measured. This effect reduces the accuracy for mercury intrusion regarding the structural information obtained from a membrane sample. The intrusion results further also include closed and blind pores. This is

the advantage of the permeance studies where only open pores contribute to the permeance of the membrane.⁴⁸ The results obtained from mercury intrusion is however still reliable and simple to obtain and represents a method that is still widely used today.

2.6.4. Membrane Surface

It was stated previously that surface roughness influences the thickness and integrity of the top-layer, and will hence have an influence on the flux of the membrane. This phenomenon has been confirmed by numerous studies.^{49, 50, 51} There are several analytical techniques that can be used to study the membrane surface. These include scanning electron microscopy (SEM), nuclear magnetic resonance (NMR), X-Ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM). Of all these techniques, SEM is the most simple to use. During SEM a physical picture of the membrane at adequately high resolution for the surface analysis is obtained of ceramic membrane supports. (Figure 2.7)

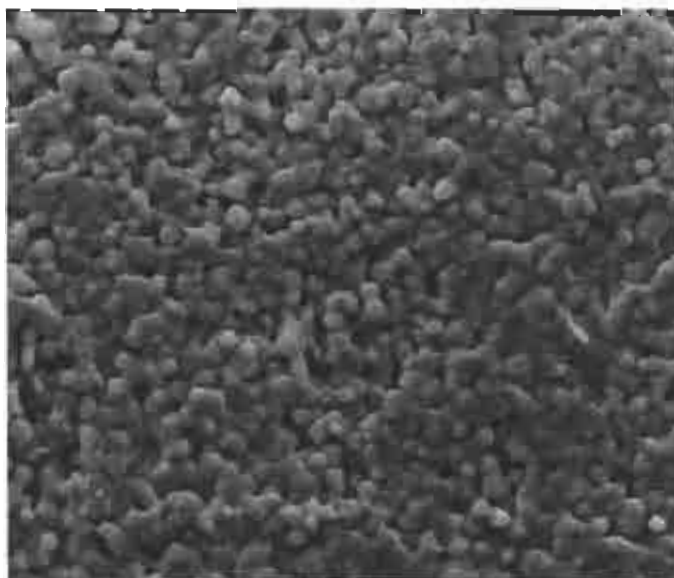


Figure 2.7. SEM photograph of nickel membrane surface

SEM can only be used to scan the surface for membrane defects and to obtain a visual impression on what the membrane surface looks like under high magnification and resolution. SEM can also be used to estimate pore size and porosity. It can further more be used to measure the top-layer

thickness if a cross-section photograph is taken. Where normal microscopy with visible light used the reflection of light by an object, SEM utilizes the scattering and emission of electrons. Through SEM, a new era was ushered into microscopy where higher magnification, increased resolution and simple operation are some of the hallmark that had made SEM a very popular research instrument. Electrons are accelerated towards an anode. Between the electron source and the anode is a column where the sample is placed. The beam of electrons is focused on a very small part of the sample, and when the electrons hit the sample it will emit secondary electrons. The electron signals can be divided into secondary electrons and backscattered electrons which are detected.

2.7. Conclusion

Since the role of inorganic membranes is apt to play an ever increasing role in industry, it is worth while to investigate the possibilities of manufacturing inorganic membranes from alternative materials.

The nickel powders that can be produced in large quantities by the hydrothermal reduction of a nickel salt with hydrazine produces spherical like particles of the appropriate size required for centrifugal dispositioning with a cost advantage over other materials. The particle properties can be varied for example by the concentration of the ethanol in the synthesis of the solution.

Membranes can be produced by dispersion processing and the sintering of the metal. Since no nickel membrane has been produced by this route to date, the membrane characterization is pivotal in portraying an image of the new membrane that has been produced. The characterization methods most commonly used include water permeance, membrane strength, mercury intrusion and SEM.

2.8. References

- ¹ J. Hofman-Zuter, Chemical and thermal stability of (modified) mesoporous ceramic membranes, Ph.D thesis, University of Twente, 1995, Chapter 2, Theoretical Background, p 9
- ² G.T.P. Mabande, G. Pradhan, W. Schwieger, M. Hanebuth, R. Dittmeyer, T. Selvam, A. Zampieri, H.Baser, R.Herrmann, A Study of Silicalite-1 and A1-ZSM-5 Membrane synthesis on stainless steel supports, *Microporous and Mesoporous Materials*, **75**, 2004, 209
- ³ P.M. Biesheuvel, V. Breedveld, A.P. Higler, H. Verweij, Graded membrane supports produced by centrifugal casting of a slightly polydisperse suspension, *Chemical Engineering Science*, **56**(11), 2001, 3517
- ⁴ G.C. Steenkamp, H.W.J.P. Neomagus, H.M. Krieg, K. Keizer, Centrifugal casting of ceramic membrane tubes and coating with chitosan, *Journal of Membrane Science*, **199**, 2002, 69
- ⁵ H. Bissett, Manufacture and optimization of tubular ceramic membrane supports, M.Sc dissertation, North West University Potchefstroom, 2005, South Africa, Chapter 3, Ceramic support optimization, p 33, 34
- ⁶ http://en.wikipedia.org/wiki/Nickel_chloride
- ⁷ M. Mulder, Basic principles of membrane technology, 2nd edition, Kluwer Academic Press, 1996, Chapter 1, Introduction, p 7
- ⁸ J.M. Benito, A. Conesa, F. Rubio, M.A. Rodriguez, Preparation and characterization of tubular ceramic membranes for treatment of oil emulsions, *Chemical Engineering Science*, **56**, 2001, 3517
- ⁹ R.M. de Vos, H. Verweij, High selectivity, high flux silica ,membranes for gas separation, *Journal of Membrane Science*, **279**, 1998, 1710
- ¹⁰ S.H. Kim, S.K. Ryi, J.S. Park, S.H. Choi, S.H. Cho, Fabrication and characterization of metal porous membrane made of Ni powder for Hydrogen separation, *Separation and Purification Technology*, **47**, 2006, 148

¹¹ S.K. Ryi, J.S. Park, S.H. Kim, S.C. Hong, D.W. Kim, Development of porous nickel membrane made by uniaxial pressing for hydrogen separation, *Desalination*, **200**, 2006, 213

¹² A. Degen, J. Macek, Preparation of submicron nickel powders by the reduction from non-aqueous media, *Nanostructured materials*, **12**, 1999, 225

¹³ <http://en.wikipedia.org/wiki/Hydrazine>

¹⁴ S.S. Park, K.H. Kim, Y.B. Lee, E.Y. Choi, H.C. Park, Synthesis of nickel powders from various aqueous media through chemical reduction method, *Materials Chemistry and Physics*, **86**, 2004, 420

¹⁵ M.M. Bettahar, R. Wojcieszak, M. Zielinski, S. Monteverdi, Study of nickel nano particles supported on activated carbon prepared by aqueous hydrazine reduction, *Colloid and Interface Science*, Article in Press

¹⁶ J.W. Park, E.H. Chae, S.H. Kim, J.H. Lee, J.W. Kim, S.M. Yoon, J.Y. Choi, Preparation of fine nickel powders from nickel hydrazine complex, *Materials Chemistry and Physics*, **97**, 2006, 371

¹⁷ <http://en.wikipedia.org/wiki/Flocculant>

¹⁸ K.S. Chou, K.C. Huang, Studies on the chemical synthesis of nanosized nickel powders and its stability, *Nanoparticle Research*, **3**, 2001, 127

¹⁹ K.H. Kim, H.C. Park, S.D. Lee, W.J. Hwa, S.S. Hong, G.D. Lee, S.S. Park, Preparation of sub-micron nickel powders by microwave assisted hydrothermal method, *Materials Chemistry and Physics*, **92**, 2005, 234

²⁰ <http://www.lsbu.ac.uk/water/hycmc.html>

²¹ H. Yu, C.F. Goh, S.S. Yong, S.G. Mhaisalkar, F.Y.C. Boey, P.S. Teo, Synthesis and cure kinetics of isotropic conductive adhesives comprising sub-micrometer sized nickel particles, *Materials Science and Engineering B*, **117**, 2005, 153

²² S.S. Park, K.H. Kim, Y.B. Lee, S.G. Lee, H.C. Park, Preparation of fine nickel powders in aqueous solution under wet chemical process, *Materials Science and Engineering A*, **381**, 2004, 337

²³ P.M. Biesheuvel, Ph.D Thesis, University of Twente, The Netherlands, 1999, Porous ceramic membranes suspension processing, mechanical and transport properties, and applications in the osmotic tensiometer

²⁴ P.M. Biesheuvel, A. Nijmeijer, H. Verweij, Theory of batchwise centrifugal casting, *AIChE Journal*, **44**, 1914

²⁵ T.P. Raming, University of Twente, The Netherlands, 1996, The stability of colloidal suspensions

²⁶ <http://en.wikipedia.org/wiki/Colloids>

²⁷ S.H. Huyn, D.H. Im, S.Y. Park, B.Y. Lee, Y.H Kim, Aqueous dispersion stability of nickel powders prepared by a chemical reduction method, *Journal of Materials Science*, **39**, 2004, 3629

²⁸ <http://en.wikipedia.org/wiki/Alumina>

²⁹ H. Verweij, P.M. Biesheuvel, Design of ceramic membrane supports: permeance, tensile strength and stress, *Journal of Membrane Science*, **156**, 1999, 141

³⁰ A. Nijmeijer, C. Huiskes, N.G.M. Sibelt, H. Kruidhof, H. Verweij, Tubular membrane supports by centrifugal casting, Laboratory for Inorganic Materials Science, University of Twente, The Netherlands

³¹ W.D. Kingery, H.K. Bowen, D.R. Uhlmann, Introduction to ceramics, Second edition, Chapter 10, 1976

³² J.S. Reed, Introduction into the principles of ceramic processing, *John Wiley & Sons*, Chapter 26 : Firing process, 1988, p 440

³³ http://en.wikipedia.org/wiki/Nickel%28II%29_oxide

- ³⁴ D.R. Lide, Handbook of Chemistry and Physics, *CRC Press Florida, USA*, 84th edition, 4-150
- ³⁵ J. Manene, The evolution of the structure of a nickel/chromium type 80/20 alloy modified by heat, *Compt. Rend*, **240**, 1955, 2413
- ³⁶ A.V. Bobrovskii, G.N.Kartmazov, V.A.Finkel, Crystal structure of nickel monoxide at high temperatures, *Izv. Akad. Nauk, USSR, Neorg. Mater*, **9(6)**, 1973, 1075
- ³⁷ K. Kim, S. Cho, K. Yoon, J. Kim, J. Ha, D.Chun, Centrifugal casting of alumina tube for membrane application, *Journal of Membrane Science*, **199**, 2002, 69
- ³⁸ E. Ferjani, M. Mejdoub, M.S. Roudesli, M.M. Chehimi, D. Picard, M. Delamar, XPS Characterization of poly(methylhydrosiloxane)-modified cellulose diacetate membranes, *Journal of Membrane Science*, **165**, 2000, 125
- ³⁹ F.C. Chen, A.J. Ardell, Fracture toughness of ceramics and semi-brittle alloys using a miniaturized disk bend test, *Innovations in Material Research*, **1**, 1996, 47
- ⁴⁰ A.S.F. Haubensak, A new method for fracture-toughness determination in brittle ceramics by open crack shake analysis, *Journal of Materials Science*, **32**, 1997, 1473
- ⁴¹ S. Gautier, E. Champion, D.B. Assollat, Rheological characteristics of alumina platelet-hydroxyapatite composite suspensions, *European Ceramic Society*, **17**, 1997, 1361
- ⁴² C. Anja, *Materials Science*, **16**, 1997, 1300
- ⁴³ M. Guazzato, M. Albakry, S.P. Ringer, M.V. Swain, Strength, fracture toughness and microstructure of a selection of all-ceramic materials, Part 1. Pressable and alumina glass-infiltrated ceramics, *Dental Materials*, **20**, 2004, 441
- ⁴⁴ <http://en.wikipedia.org/wiki/hardness>
- ⁴⁵ <http://www.mindat.org/min-801.html>

⁴⁶ http://www/mcelwee.net/html/hardness_comparisons.html

⁴⁷ J. Zah, H.M. Krieg, J.C. Breytenbach, Pervaporation and related properties of time-dependent growth layers of zeolite NaA on structured ceramic supports, *Journal of Membrane Science*, **284**, 2006, 276

⁴⁸ A. Jena, K. Gupta, Porosity characterization of microporous small ceramic components, *Porous Materials Inc*, 2001

⁴⁹ K. Riedl, B. Girard, R.W. Lencki, Influence of membrane structure on fouling layer morphology during apple juice clarification, *Journal of Membrane Science*, **139**, 1998, 155

⁵⁰ M. Elimelech, X. Zhu, A.E. Childress, S. Hong, Role of membrane surface morphology in colloidal fouling of cellulose acetate and composite aromatic polyamide reverse osmosis membranes, *Journal of Membrane Science*, **121**, 1996, 209

⁵¹ M. Hirose, H. Ito, Y. Kamiyama, Effect of skin layer surface structures on the flux behaviour of RO membranes, *Journal of Membrane Science*, **121**, 1996, 209

Chapter III

Experimental – Nickel membrane manufacture

3.1. Nickel powder manufacture

3.1.1. Hydrothermal reduction procedure

The nickel powders were prepared using conventional laboratory equipment. According to Kim *et al* ^{1, 2, 3} and Degen and Macek ⁴, solid nickel particles can be precipitated by means of the reduction of a nickel salt in polar or non-polar systems, in the presence of a strong reducing agent like hydrazine. The experimental procedure was modified to fit our requirements and is given as a flowchart in Figure 3.1.

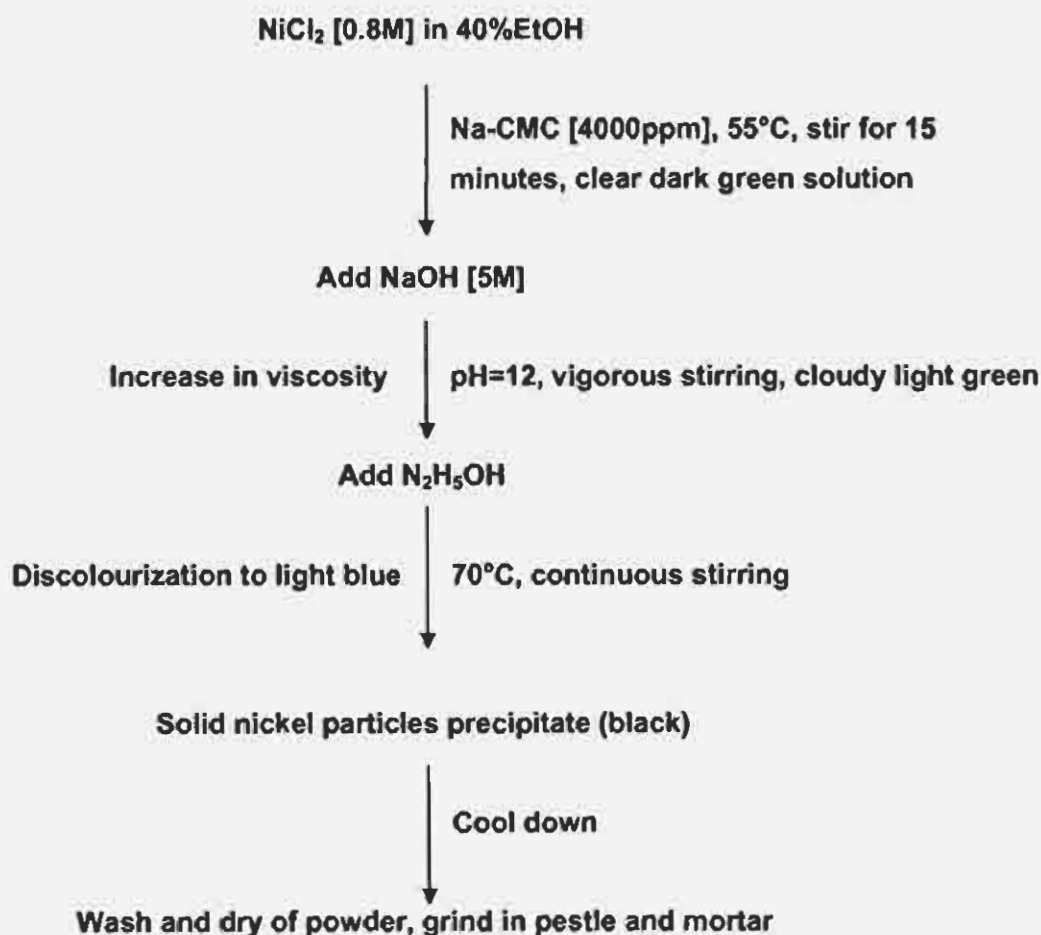


Figure 3.1 Schematic representation of nickel powder manufacture and purification

200 g of nickel chloride hexahydrate - $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ - (Aldrich Chemical Corp, Germany) was dissolved in 600 ml of deionised water. Absolute ethanol (400 ml) was added to make a 0,8 M NiCl_2 solution in 40% EtOH. The nickel powders must be kept as non-magnetic as possible, as this will lead to agglomeration. The solution was stirred until all the $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ powder was dissolved (approximately 15 to 20 minutes). Four gram of sodium-carboxymethylcellulose (Na-CMC) (Fluka Chemical Corp, Germany) was added to the solution to constitute a 4000ppm concentration. The Na-CMC was added slowly to prevent clotting of the chemical. The Na-CMC acts as an antiflocculant⁸ and prevents large agglomerates from forming during the precipitation process. The solution was then stirred for a further 10 minutes to ensure all the Na-CMC had dissolved in the water. After addition, the $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ solution was heated on a non-magnetic hotplate. Simultaneously NaOH (Merck Chemical Corp, Germany) [5M] was added to the solution, until the pH of the solution reached 12 and the solution became a thick green slurry. A Meterohm digital pH meter (model 744) was used to measure the pH. The NaOH was prepared by stirring and dissolving 200 g NaOH pellets in 1000 ml deionised water. The adjustment of the pH to 12 plays a double role as it increases the viscosity of the slurry because of the expansion of the polymer (Na-CMC) sidechains, and sets the stage for the reduction procedure to follow, where a very basic environment is required.^{1, 2, 3, 4}

Vigorous mechanical stirring is required whilst the slurry is heated on the hotplate. When the temperature of the slurry reached 55°C, hydrazine hydrate - $\text{N}_2\text{H}_5\text{OH}$ - (Aldrich Chemical Corporation, Germany) was added to the slurry. The hydrazine had a chemical purity >98%, and a concentration of 65% (m/v). According to Park *et al*^{1, 2, 3} the molar ratio of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$: $\text{N}_2\text{H}_5\text{OH}$ used in these preparations should be 1:2. Thus, for 200g of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, which constitutes to ≈ 0.8 mole of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 1.6 mole of $\text{N}_2\text{H}_5\text{OH}$ should theoretically be added to the slurry in order for the precipitation reaction to be initiated. Thus if 51.2ml of pure hydrazine is required theoretically, 80 ml of the 65% hydrazine is added to introduce 51.2ml of hydrazine into the system. The addition of hydrazine to the system lead to an exothermic reaction, increasing the temperature of the slurry to 60°C. After about 5 minutes, the green colour darkened because of the precipitation of the nickel particles. After another 10 minutes, the slurry had turned completely black because of the formation of large quantities of nickel particles. This was accompanied by continuous stirring of the slurry. Whilst the reaction is progressing, the temperature increases rapidly, until it is controlled to be about 70°C by reducing the temperature of the hotplate, where it will stay for the remainder of the precipitation reaction. The onset of the reaction is indicated by the formation of ammonia (NH_3) gas. It took approximately another 45 minutes for the reaction to complete, indicated by the cessation of the formation of ammonia gas. After the system had cooled down to room temperature, a black nickel precipitate remained, covered by a clear supernatant.

3.1.2. Powder purification and preparation for dispersion formulation

After the precipitation reaction of the newly formed nickel power, it had to be cleaned to prepare it for dispersion and membrane manufacture. The clear supernatant was drained. Hereafter, the powder or pellet was redispersed in 1500 ml deionised water. This was accompanied by vigorous mechanical stirring, and reheating (80°C) of the dispersion, in order to promote the removal of exipients used in the preparation of the nickel powder. After several minutes the dispersion was allowed to cool back to room temperature. The new supernatant was drained and the process repeated. This whole process was repeated three times to ensure that no other impurities remained with the nickel powder. After the final drainage, the powder was placed in an oven at 120°C for 6 hours to remove all moisture from the nickel powder.

Subsequently the powder was removed from the Pyrex beaker using a hard brush, whereafter it was grinded in a pestle and mortar for 20 minutes to the final product. The pestle and mortar was thoroughly cleaned with diluted hydrochloric acid (HCl) prior to the milling of the nickel powder. The final product was kept in 200 ml plastic air tight containers (Kartell®, Italy). Four different powders were prepared with varying ethanol concentration ranging from 10% (v/v) to 40% (v/v).

3.2. Powder characterization

In order to characterize and determine the quality of the nickel powders produced, the following characterization techniques were used.

3.2.1. Particle size analysis

According to the method of Kim *et al*^{1, 2, 3}, the nickel particles precipitated have a mean particle size of 0.3 µm and larger. Thus, SEM could be used to measure the average particle size. A laser particle size analyzer (Malvern Mastersizer, UK) was also used to confirm the average particle size and particle size distribution. No palladium coating was applied to the nickel particles, and all particles were analyzed by SEM as is. A FEI Quanta 200 ESEM was used.

3.2.2. EDS analysis

The composition of the nickel powders was analyzed using EDS incorporated into the FEI Quanta ESEM.

3.2.3. XRD analysis

To verify the production of nickel particles and to determine the crystal phase, the nickel powders were analyzed by X-ray diffractometry (XRD). The instrument used was a Siemens D-501 X-ray Diffractometer with Co K α radiation. Analysis was carried out on unsintered powders.

3.3. Dispersion formulation

In this study, the effects of three polymers on dispersion stability were studied. They include:

- Ammonium polymethacrylate (Darvan C®) (APMA)
- Polyvinylpyrrolidone (PVP)
- Polyacrylamide-co-diallyldimethylammoniumchloride (PAAco)

Both polyvinylpyrrolidone (PVP) with an Mw of 1.3×10^6 g.mol⁻¹ and the polyacrylamide co-diallyldimethylammoniumchloride (PAAco) with a stock concentration of 10% (w/v), were purchased from Aldrich Chemical Corporation, Germany. No further purification was carried out on these polymers. The PVP was dissolved in deionised water to obtain a stock concentration of 0.5% (v/v), while the PAAco was diluted in deionised water to a concentration of 0.5% (v/v). Two sets of experiments were carried out namely the determination of the effectivity of the three polymers in dispersing the nickel particles and secondly the formulation of the nickel particles for centrifugal dispositioning.

3.3.1. Dispersion stability

To measure the ability of the three different polymers to stabilize the nickel dispersion, the transmission of light through the dispersion with variable concentrations of the three polymers were measured over time. The experiments were carried out using a Varian® Cary 50™ UV-vis Spectrophotometer. The instrument was set at a fixed wavelength of $\lambda = 1100$ nm in single beam mode. A blank was taken of each of the polymers dissolved in water, at each corresponding concentration to eliminate the possibility of light absorption by the polymer.

Five different concentrations (0.01% (v/v) – 0.25% (v/v)) of the three different polymers (PAAco, PVP, APMA) were used to determine the effectivity of each polymer in stabilizing the nickel powders in dispersion. The spectrophotometer was set to record transmission values every 12 seconds for 2 hours. The concentration of the nickel particles used in the light dispersion quantification experiment was $0.25 \text{ g} \cdot 100\text{ml}^{-1}$.

3.3.2. Dispersion formulation for membrane manufacture

To disperse the nickel powders into a thick slurry, a 500ppm concentration of PAAco in deionised water was used to stabilize the dispersion. To produce membranes of the desired thickness and dimensions, a dispersion containing 72% (m/v) nickel particles was prepared. 52 g Nickel powder was added to 80 ml of 0.5% (v/v) PAAco. After the required amount of PAAco had been added to the nickel powder, the dispersion was vigorously agitated (mechanically) to ensure that all the nickel particles were covered with sufficient amounts of polymer. This procedure was carried out for 6 hours using a mechanical arm shaker with variable rate control at 50% speed. The dispersion was prepared in plastic 200 ml Kartell® containers.

3.4. Centrifugal casting

After optimizing the dispersion formulation, the next step entailed the centrifugal dispositioning of the nickel powder, to obtain a green casted membrane. The custom built centrifuge used, is shown in Figure 3.2. Before the dispersion was centrifuged, the inside surface of the stainless steel moulds (before being coated with liquid paraffin dissolved in petroleum ether ($5 \text{ g} \cdot 100\text{ml}^{-1}$)), was washed with water and dishwashing liquid and scrubbed with a hard brush. The moulds were dipped twice. After the coating, the dispersion of nickel powders was poured into the mould and centrifuged at 12000rpm for 10 minutes. The speed of the centrifuge was accurately controlled with a voltage regulator. The flow rate of nitrogen gas (used for the cooling of the centrifuge bearings) was maintained at 150 kPa. After centrifugation the remaining polymer solution (supernatant) was carefully sucked from the cast (after the plastic plugs had been removed (slowly and carefully)).

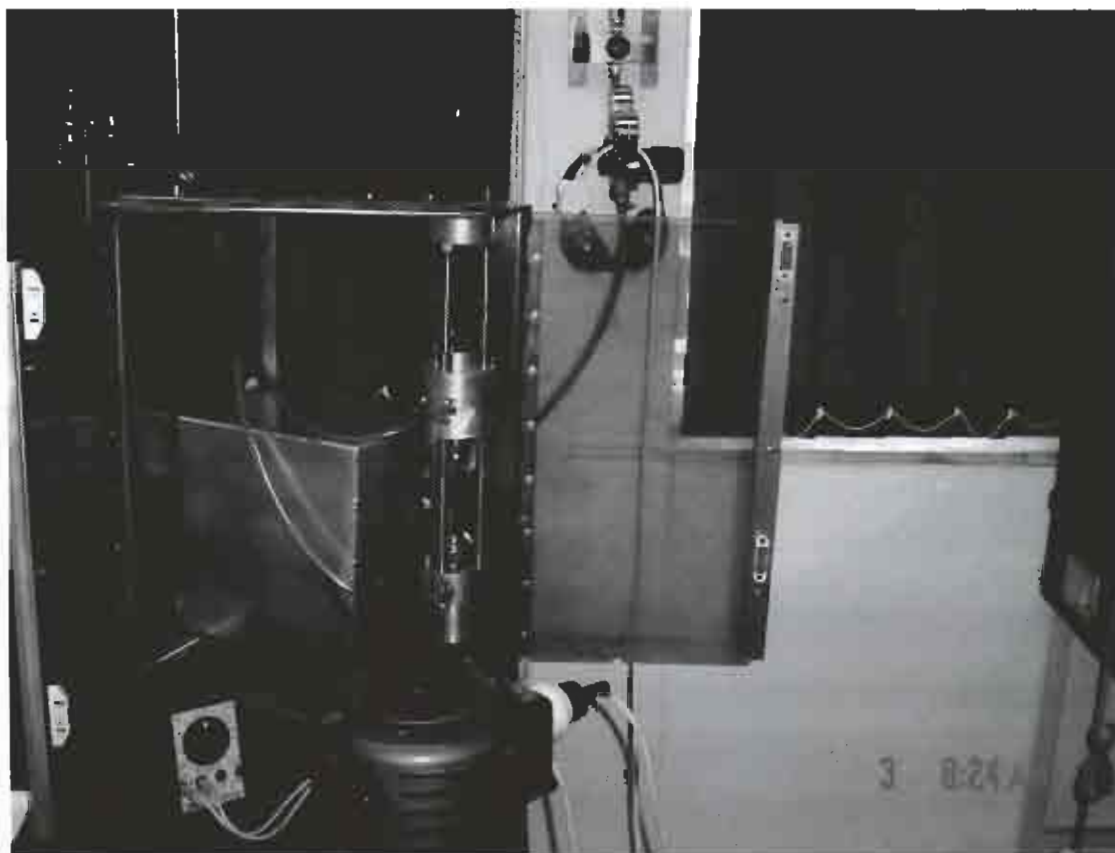


Figure 3.2. Custom built centrifuge

3.5. Sintering

After centrifugation, the green-casted membrane was dried in an oven at 30°C for 12 hours whilst still remaining in the stainless steel mould. The membrane was then removed from the cast and sintered vertically or horizontally depending on the oven used. A temperature range spanning from 950°C to 1250°C was used to sinter 7 membranes at 50°C increments. For sintering temperatures ranging from 950°C to 1200°C a Carbolite CWF 1200 (Sheffield, UK) was used to sinter the supports. For 1250°C, a Carbolite CWF 1600 (Sheffield, UK) oven with a maximum temperature of 1600°C was used. In the latter oven, the membrane was sintered horizontally since the oven is a horizontal tube furnace. In the case of the CWF1200, membranes were sintered vertically. The sintering programme followed for all membranes were as follow (as presented in Figure 3.3):

- Ramp from 25°C to 420°C at a rate of 0.4°C/min
- Maintain at 420°C for 60 minutes
- Ramp from 420°C to the appropriate sintering temperature at 0.8°C/min
- Sinter for 60 minutes at specific sintering temperatures
- Deramp from sintering temperature to 25°C at 1.2°C/min

After the sintering programme ended, the membranes were characterized.

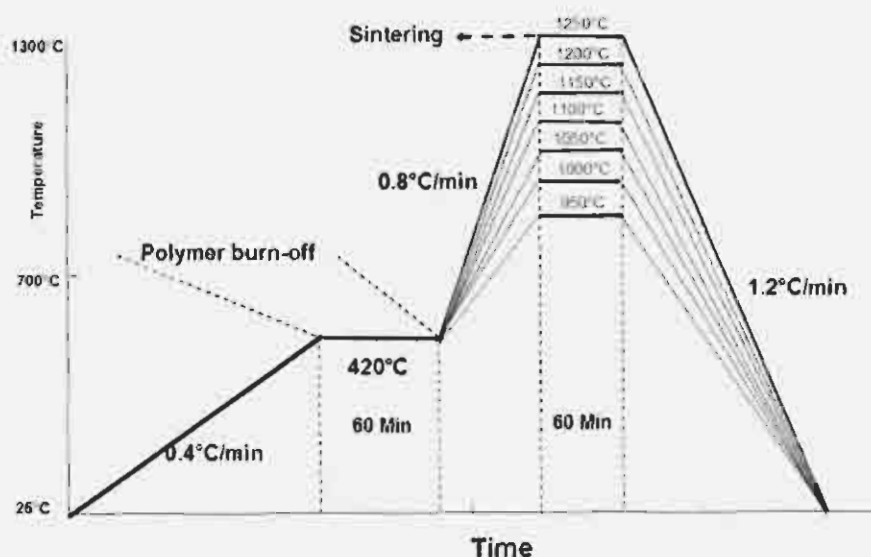


Figure 3.3. Graphical representation of the sintering programme

3.6. Membrane characterization

3.6.1. Dimensions and shrinkage

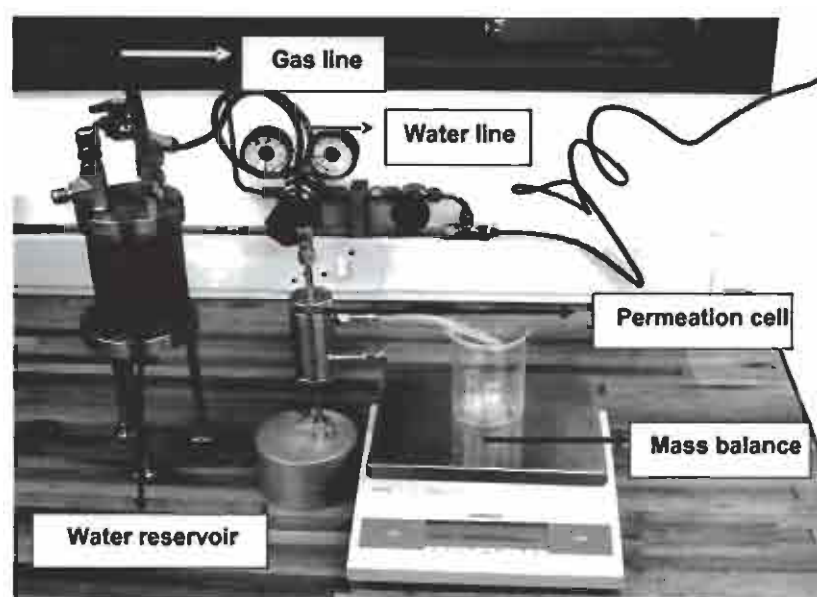
The outer and inner diameter and the length of the membranes were measured before and after every sintering to determine the degree of shrinkage of the sintered membranes. Dimensions of the membrane were measured and compared to the initial dimensions of the membrane as it was spun up in the casts. A Veneer Caliper was used for the measurements.

3.6.2. Mercury Porosimetry

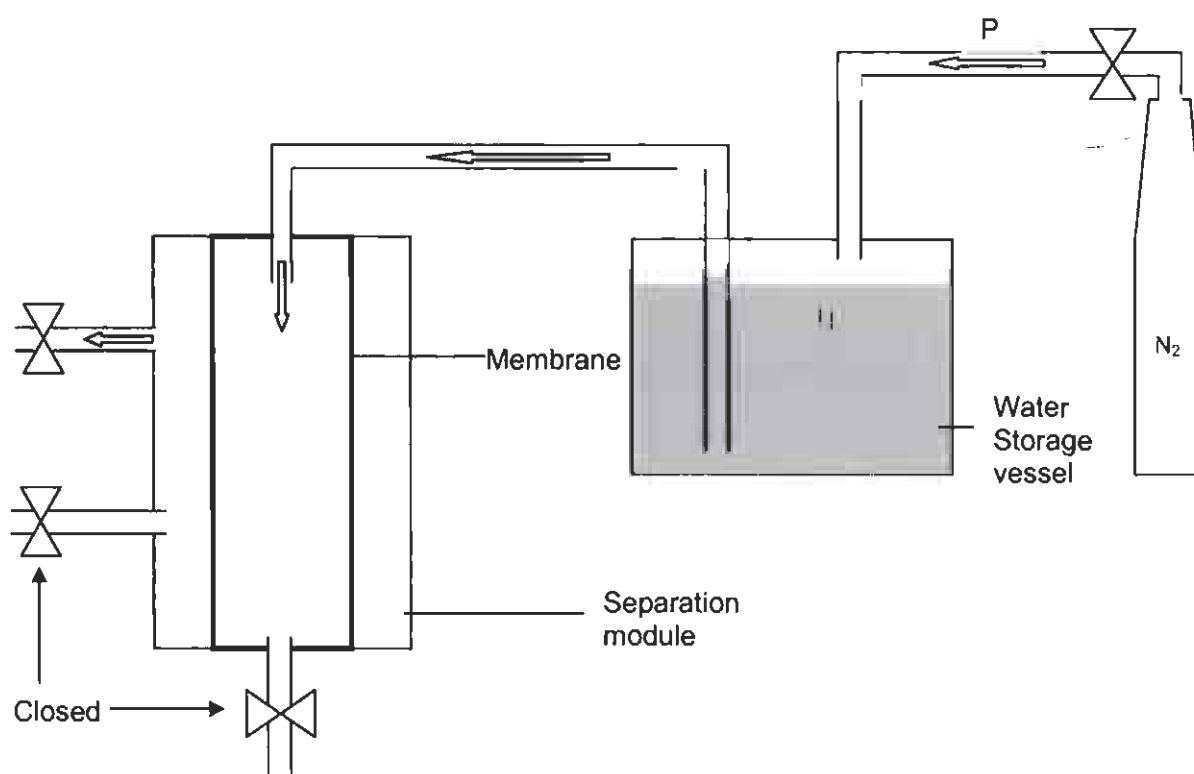
To determine the mean pore radii, pore size distribution and porosity of the sintered membranes, mercury porosimetry (Autopore III, Micromeritics, USA) was carried out on samples of the membranes. All samples were pre-prepared by drying at 120°C for 6 hours to ensure that all moisture had been removed from the cavities of the membrane samples. A penetrometer with part nr 942-61707-00 and a total stemvolume of 0.392 ml was used.

3.6.3. Water permeance

To test the water permeance of the nickel membranes, a setup consisting of N₂ gas supply, water storage vessel and separation module was used to carry out the experiments (Figure 3.4). N₂ gas was used as the driving force to apply the required pressure on the deionised water forcing it through the support. The membrane was sealed in the separation module using o-rings. A dead end mode was used for the separation characterization. A mass balance was used to determine the flow of water through the membrane. The volumetric flow rate was determined at different pressures (2-10 bar), converted to flux and plotted against the pressure. From the slope of the straight line the permeance was obtained for each membrane.



(a)



(b)

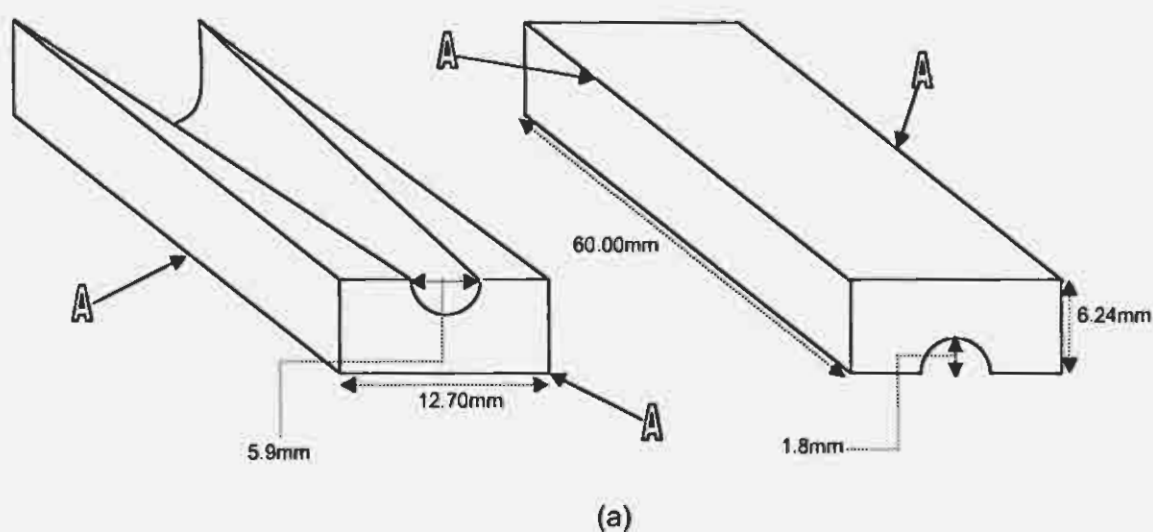
Figure 3.4. A visual (a) and schematic (b) representation of the water permeance setup

3.6.4. SEM

Scanning Electron Microscopy (SEM) was utilized to study the membrane surface and cross section under high magnification and contrast. For this purpose a FEI Quanta ESEM instrument was used. Photographs of the inner side as well as cross sections were taken.

3.6.5. Membrane strength

To determine the strength of the membranes, a novel apparatus was used to exert pressure from the inside of the membrane (Figure 3.5).⁵ A cone shaped structure is inserted in the inside of the membrane, and by pressing the cone deeper, the pressure on the inside is increased. The force required for membrane to break or rupture the membrane was measured using a tensometer type W (A.R. Adams trading).



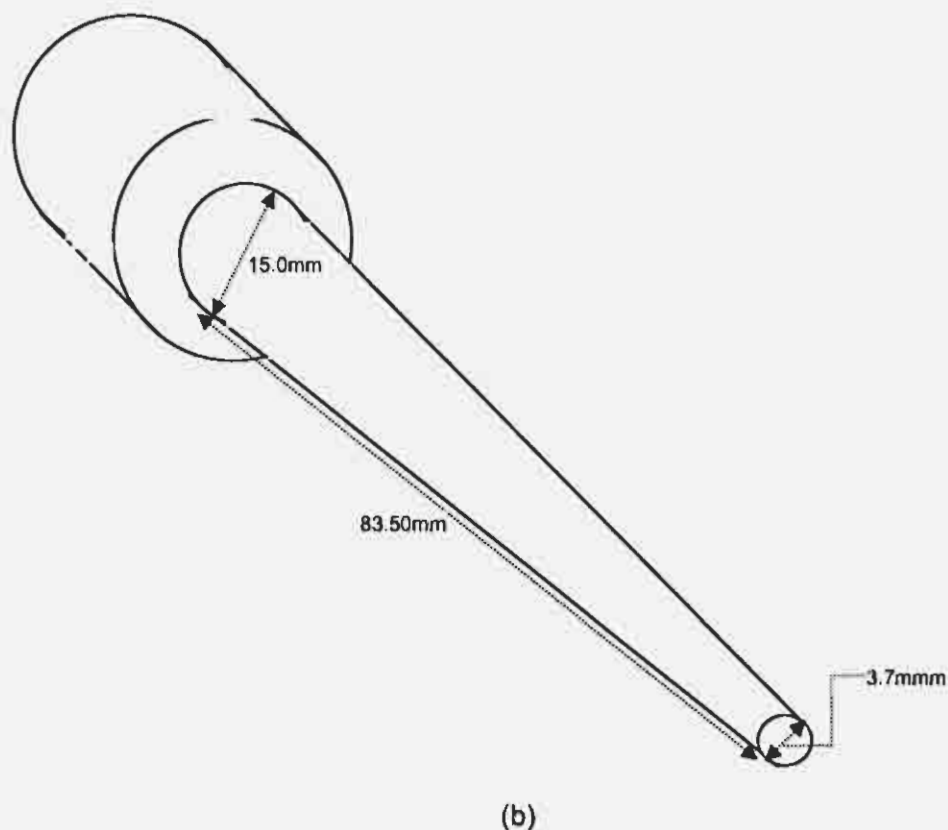


Figure 3.5. Strength testing apparatus with conical cavities (a) and cone (b)⁵

According to the design, only the metal pieces marked 'A' were in contact with the support structure. To determine the force applied on the wall of the membrane the following equation was used to convert force to pressure:

$$\text{Pressure (Pa)} = \frac{\text{Force (Newton)}}{\text{Area (m}^2\text{)}} \quad (3.1)$$

The contact area 'A' was calculated according to:

$$\text{Area} = L \times w \quad (3.2)$$

where w is the width in mm and L is the length of the contact section in mm, which is equivalent to the length of the membrane.

3.7. References

- ¹ K.H.Kim, Y.B. Lee, E.Y.Choi, H.C.Park, S.S.Park, Synthesis of nickel powders from various aqueous media through chemical reduction method, *Materials Chemistry and Physics*, **86**, 2004, 420
- ² K.H.Kim, Y.B.Lee, S.G.Lee, H.C.Park, S.S.Park, Preparation of fine nickel powders in aqueous solution under wet chemical process, *Materials Science and Engineering A*, **381**, 2004, 337
- ³ K.H.Kim, H.C.Park, S.D.Lee, W.J.Wha, S.S.Hong, G.D.Lee, S.S.Park, Preparation of submicron nickel powders by microwave-assisted hydrothermal method, *Materials Chemistry and Physics*, **92**, 2005, 234
- ⁴ A.Degen, J.Macek, Preparation of submicron nickel powders by the reduction from non-aqueous media, *Nanostructured materials*, **12**, 1999, 225
- ⁵ H.Bissett, Manufacture and optimization of tubular ceramic membrane supports, M.Sc dissertation, North West University Potchefstroom, 2005, South Africa, Chapter 3, Ceramic support optimization

Chapter IV

Results and Discussion

4.1. Introduction

According to literature, nickel powders produced by Degen and Macek ¹ have a uniform particle size distribution, and a suitable average particle size for centrifugal dispositioning.² The size of the particles ranges from 150µm – 1200µm which is typically suitable for the manufacture of microfiltration membranes. The purity of the powder is usually high and all particles are more or less spherical shaped. It should however be noted that it is difficult to manufacture inorganic membranes by centrifugal casting, since the technique requires that a powder is both homogeneous in size and homogeneously dispersed. Non-adherence will result in misformed membranes, irregular membranes, and membrane breakage. Both the powder and the dispersant are thus of vital importance when producing membranes that are of superior quality³

The disadvantages of nickel are apparent when taking in consideration the nature of the metal. Elementary nickel is soft, deforms plastically, is susceptible to oxidation and is acid labile.⁴

4.2. Nickel powder manufacture

4.2.1. Nickel precipitation reaction

The initial mixture of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, NaOH, EtOH produced a clear bright green mixture in the first experimental step (Figure 3.1) where after the following steps were adhered to. The $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ had to be stirred vigorously because of the relatively low solubility of the salt in the EtOH / H_2O solution. The Na-CMC had to be added slowly to the solution to prevent the polymer from forming large clots which are not easily dissolved in the solution. By adding the Na-CMC slowly, the exposed surface area of the Na-CMC is increased facilitating its solubility. Thirdly, the heating of the solution had to be controlled very carefully, especially after the NaOH had been added. Due to uneven heating of the solution, the erratic boiling caused spillage and the experiment had to be terminated. The addition of the NaOH (Figure 4.1) to the solution caused the solution to turn viscous because of the presence of Na-CMC, the latter's viscosity being sensitive to changes in pH.⁵

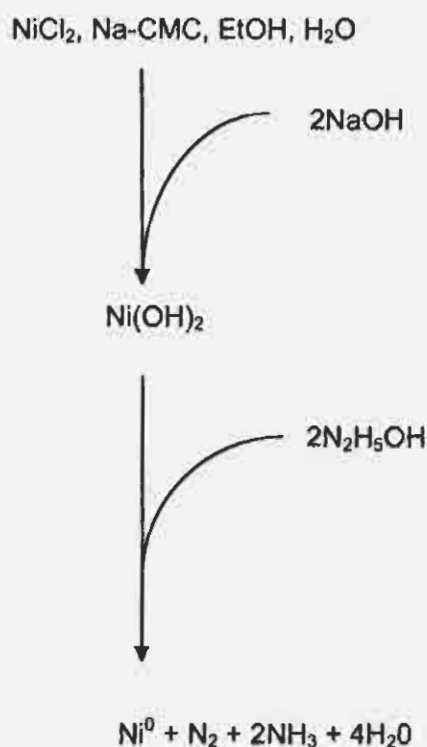


Figure 4.1. Precipitation and complex formation of nickel from nickelchloride and hydrazine

The subsequent addition of hydrazine hydrate ($\text{N}_2\text{H}_5\text{OH}$) to the mixture resulted in the NiCl_2 (Figure 4.1) being converted to Ni(OH)_2 (purple) which coloured the solution from its bright green to a darker, bluish green. The addition of hydrazine also caused a slight decrease in the rate of evaporation of the EtOH. After about 5 minutes, the solution turned black (Figure 4.2). This was because of the nickel particles precipitating from the Ni(OH)_2 . This was confirmed by (a) dipping a magnet into the slurry of nickel particles and removing some of the particles, and (b) by the formation of NH_3 gas. After every synthesis (duration: 60 minutes), a black nickel precipitate remained at the bottom of the beaker. After drying, the precipitate was weighed and had an average weight of 51.8 g ($n = 10$). Thus for every 200 g of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, an average 51.8 g of pure nickel powder was produced. This calculates to a quantitative conversion in terms of the Ni^{2+} being converted to Ni(s) . The amount of hydrazine added to initiate the precipitation reaction also had considerable effects on the precipitation reaction. If too little hydrazine was added (< 1.6 mol), the reaction would not commence. If too much hydrazine was added to the solution (> 3.5 mol), a snowball effect was initiated, because the newly formed nickel particles act as catalysts by

producing NH_3 (g) from the remaining hydrazine. Increased concentrations of hydrazine accelerated this reaction to such an extent that it leads to a violent reaction, causing the nickel slurry to foam excessively over the side of the beaker. It is thus important to adhere to the prescribed hydrazine, nickelchloride ratio of 2:1.^{1,6}

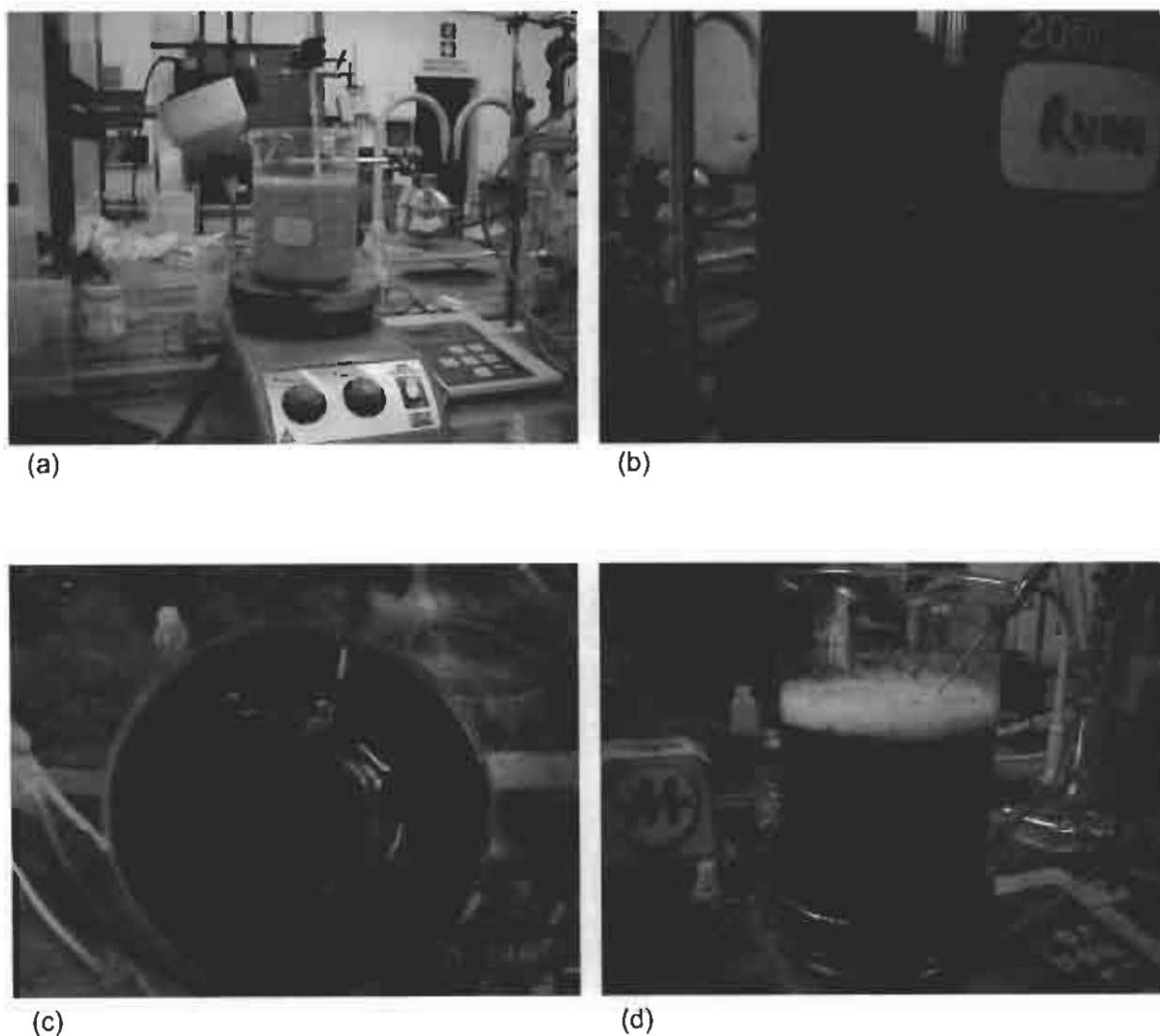
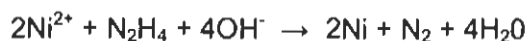
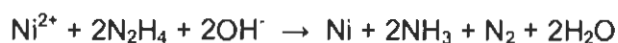


Figure 4.2. Photographs of the (a) initial solution of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ which is light green, (b) (c) after the addition of hydrazine hydrate to the solution where both nano-sized nickel particles and $\text{Ni}(\text{OH})_2$ are present, and finally (d) the completed reaction with the precipitated nickel

According to literature the formation of Ni^0 can be expressed in terms of the following reaction equation:⁷



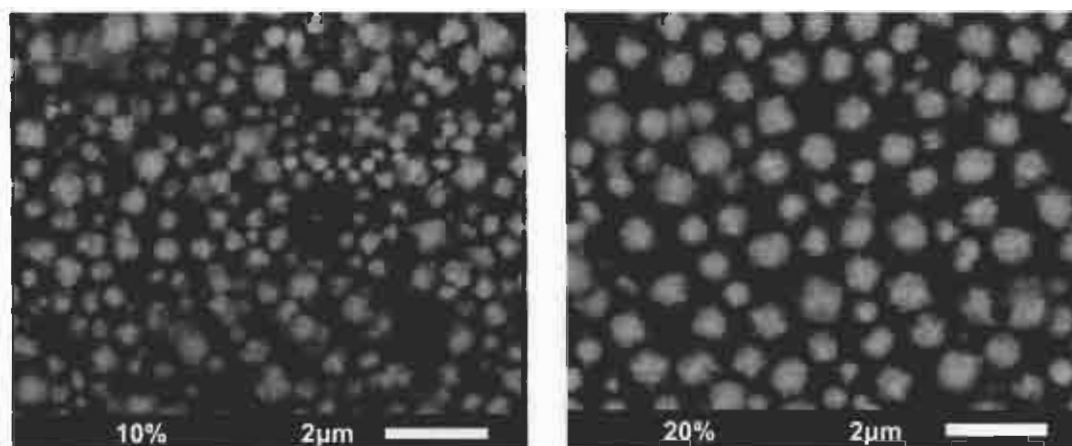
However, during the experimental manufacture of the particles, the unmistakable smell of NH_3 meant the reaction route was slightly different under these specific experimental conditions. To make provision for the production of NH_3 , we thus propose the following reaction equation:



It is clear from Figure 4.3 of the formation of dendrites (spikes) on the outer surface of the nickel particles, which confirms the formation of nickel particles by nucleation.⁸

4.2.2. Influence of EtOH concentration

Since ethanol influences the particle size which has a profound influence on membrane manufacture and its properties, particles were manufactured using variable ethanol concentration. It was found from varying the ethanol concentration had a pronounced influence on the particle size and particle size distribution. It should be noted that the largest possible particle size that can be used to manufacture the membranes by centrifugal dispositioning will lead to an increase in porosity, pore size and hence permeance. The powders were analyzed with SEM to determine the increase in the particle size. In Figure 4.3, the SEM photos of the particles obtained at different ethanol concentrations are presented. The spiky surface of the individual particles indicates a spherulite structure. This is in agreement with Tashiro *et al* who described the surface morphology as having a dendrite structure.



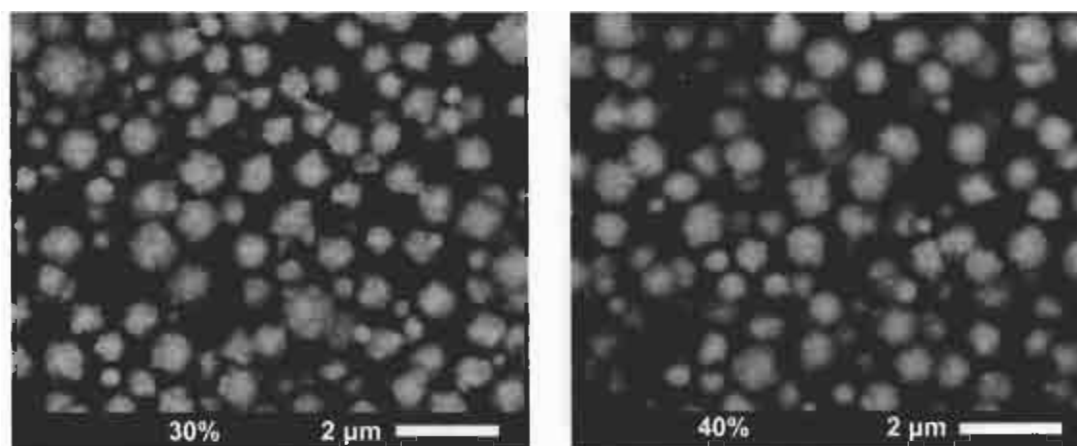


Figure 4.3. SEM photographs of nickel particles produced with (a) 10% EtOH, (b) 20% EtOH, (c) 30% EtOH, and (d) 40% EtOH

It can be seen that an increase in ethanol concentration lead to an increase in the average particle size. Four experiments were done with 10, 20, 30, and 40% EtOH (v/v). The 10% (v/v) solution produced powders with the smallest mean particle size, while the 40% (v/v) produced the powders with the largest particle sizes, with the 20% and 30% (v/v) in between. The size of a large number of particles was measured using SEM, the average obtained for each ethanol concentration and plotted as a function of the ethanol concentration (Figure 4.4). The standard deviation for the SEM measurements was approximately 20%. (See Table 4.1)

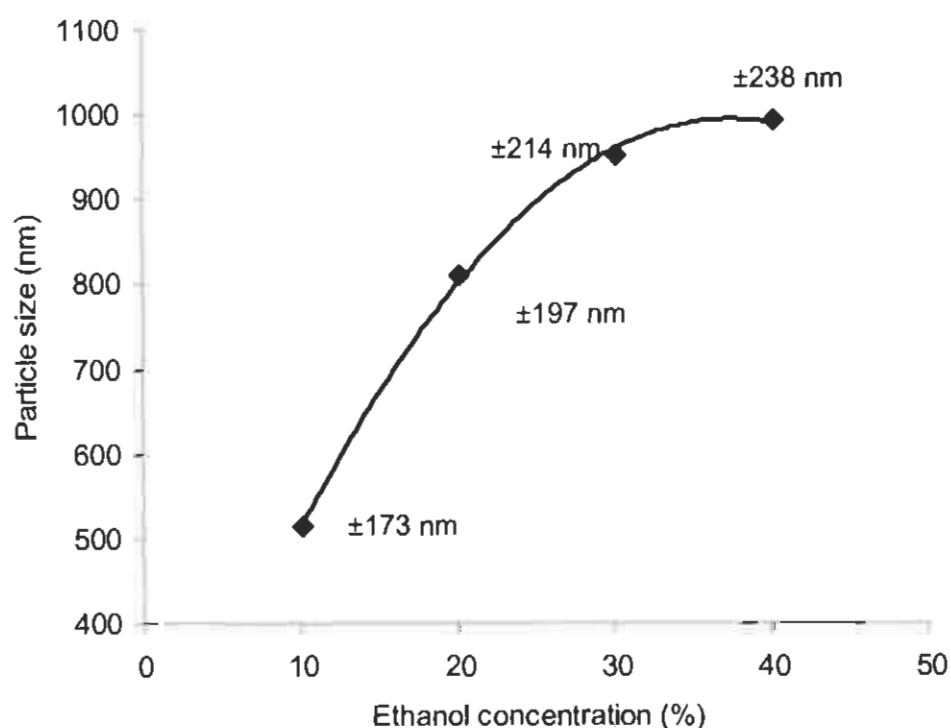


Figure 4.4. Particle size as a function of ethanol concentration (error included)

It is clear from Figure 4.4 that the increase in particle size with increasing ethanol concentration levels at 30% (v/v) EtOH. It seems that the increase in particle is related to the decrease in the water concentration with increasing ethanol concentration which could result in decreased solubility of the NiCl_2 and hence more product being formed. This was confirmed in terms of the yield of Ni(s) which increased from 49.5 g in 10% (v/v) EtOH to 51.8g in 40 % (v/v) EtOH. The direct proportionality observed is contrary to the findings of Kim *et al*^{9, 10} who also investigated the variations in particle size with changes in ethanol concentration. They found that an increase in ethanol concentration lead to a decrease in the mean particle size. They however, used a similar argument stating that the addition of an alcohol will lead to a reduction in the solubility of NiCl_2 , which will lead to a reduction in the dielectric constant of the solution. In turn, the decrease of the dielectric constant will result in the reduction of the surface energy of the newly formed nickel particles and thus alter the reaction and coalescence rate of the particles. This seems to imply that while the higher EtOH resulted in smaller particles but probably more particles under the experimental conditions used by Kim *et al*, in our case it resulted in more deposition of Ni on the available particles, resulting in an increase of the particle size with increasing ethanol concentration. Another attempt to explain the influence of EtOH on particle size was given by Tashiro *et al*.¹¹ According to their findings the increase in the ethanol concentration results in a decrease in the reduction capability of hydrazine, which will reduce the nucleation rate and thus the amount of nuclei formed, resulting in the formation of larger particles. This concurred to the increase in particle size with increasing ethanol concentration, found in our study. For manufacturing powders for centrifugal dispositioning, an ethanol concentration of 40% (v/v) was used, since it produced the largest powders which were still suitable for centrifugal casting and membrane manufacture.

4.2.3. Nickel powder purification

To produce the nickel powder in such a way that it will be fit for centrifugal dispositioning, the powders had to be cleaned in a specific way. Failure to do so lead to large scale agglomeration of the nickel particles, as described in Section 4.2.4. The nickel particles were washed three times consecutively in deionised water. It was found that boiling the particles for 15 minutes in water during each wash, produced powders with improved dispersion ability and smoother inner membranes surfaces, since the solubility of impurities like Na-CMC and NaCl increased. The

milling in the pestle and mortar (15 minutes) further promoted the formation of a finer, less agglomerated nickel powder.

4.2.4. Nickel particle agglomeration

An unpleasant (because unwanted) characteristic of Ni(s) which became apparent during the initial nickel precipitation experiments, was that the nickel particles were highly ferromagnetic. This characteristic lead to the particles being attracted to each other, leading to large agglomerates and hence to the destabilization of the dispersion stability. The manufacturing procedure had to be altered to produce powders that had a minimum magnetization of Ni particles. This was achieved by avoiding a magnetic field and magnetic stirrer during the precipitation reaction. Since the reaction had to be carried out with continuous stirring of the solution , alternative methods had to be considered to ensure continuous stirring. The experiment was thus carried out using mechanical stirring, i.e. by hand. Another cause of agglomeration was chemical agglomeration due to (a) the formation of NaCl crystals and (b) the agglomeration of nickel particles by the remaining Na-CMC. In Figure 4.5. a light microscopy photograph is presented where the agglomerates and NaCl crystals can clearly be seen.

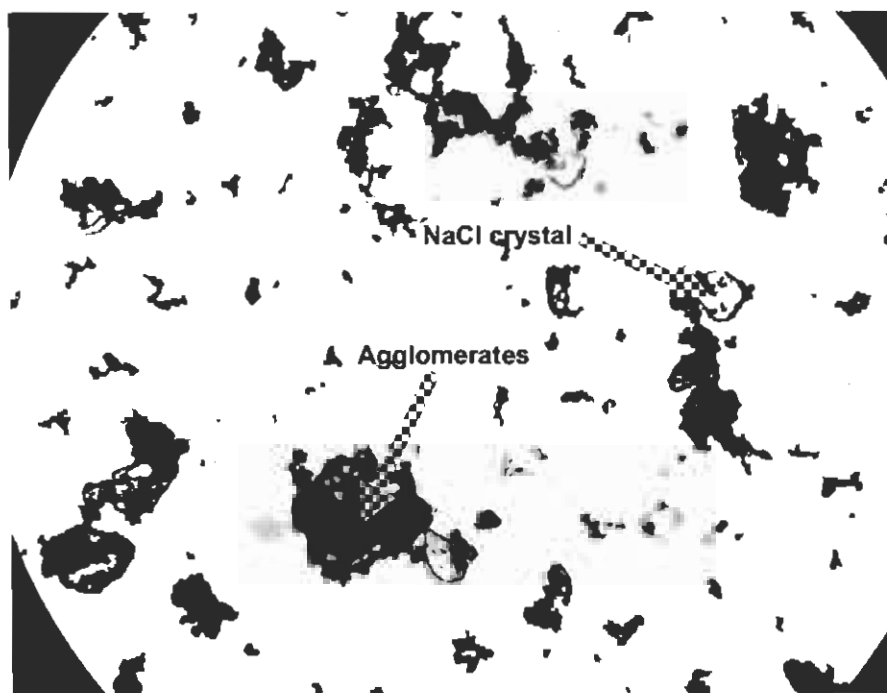


Figure 4.5. Light microscopy photograph of agglomerated nickel particles (before washing) due to magnetic and chemical agglomeration

4.2.5. Powder Characterization

4.2.5.1. Particle size

It was stated in the previous section how important the washing was for membrane manufacture. Washing was as important for the powder characterization, specifically for the determination of particle size, particle size distribution and composition by laser diffraction. Particle analysis by means of SEM is in a sense simpler because readings are not distorted by chemical or magnetic agglomeration. Unfortunately, analysis by means of SEM is not as accurate, because only a small fraction of the powder is analyzed, and the powder size is measured with a digital ruler where visual errors may occur. The experimental error of the data presented in Section 4.2.3 was calculated, and is given in Table 4.1. However, in spite of the large variation, the particle size analysis by SEM is still more accurate than the laser analysis, because the particles can be physically seen and particle agglomeration can therefore be identified and ignored.

Table 4.1. Mean particle size and experimental error as determined for particle size analysis on nickel powders analyzed by SEM. (See Figure 4.4)

% EtOH	Mean Particle size $\pm$ Error
10 %	0.51 μm $\pm$ 0.17 μm
20 %	0.81 μm $\pm$ 0.20 μm
30 %	0.95 μm $\pm$ 0.20 μm
40 %	1.02 μm $\pm$ 0.24 μm

In Figure 4.6, the percentage volume of the particle size distribution of the powder manufactured with 40% EtOH (v/v) as a function of particles size is given (a) before and (b) after cleaning when mechanical stirring was used. The four lines in each graph show the repeatability of the analysis. The large peak at 100 μm before cleaning (Figure 4.6 (a)) is due to chemical agglomerates and the smaller peak at 4 μm seems to indicate magnetic agglomerates. The large peaks represents

agglomerates formed because of impurities, for example Na-CMC which encapsulated the fine nickel particles (chemical agglomeration). This is confirmed by Figure 4.6 where the chemical agglomerates have been removed but the magnetic agglomerates endured. Interestingly the washed powder gave another peak at $0.1\mu\text{m}$ which could not be confirmed by SEM.

While it was fairly simple to remove the chemical agglomerates by washing and boiling, removing the magnetization of the nickel powders was more difficult, even when precipitation took place under non-magnetic conditions. The nickel particles are attracted to each other to form large agglomerates which impaired the ability of the Malvern to quantify the particle size and its distribution. It is therefore clear that size analysis by laser diffraction in a dispersion is not feasible for hydrothermally prepared nickel powders.

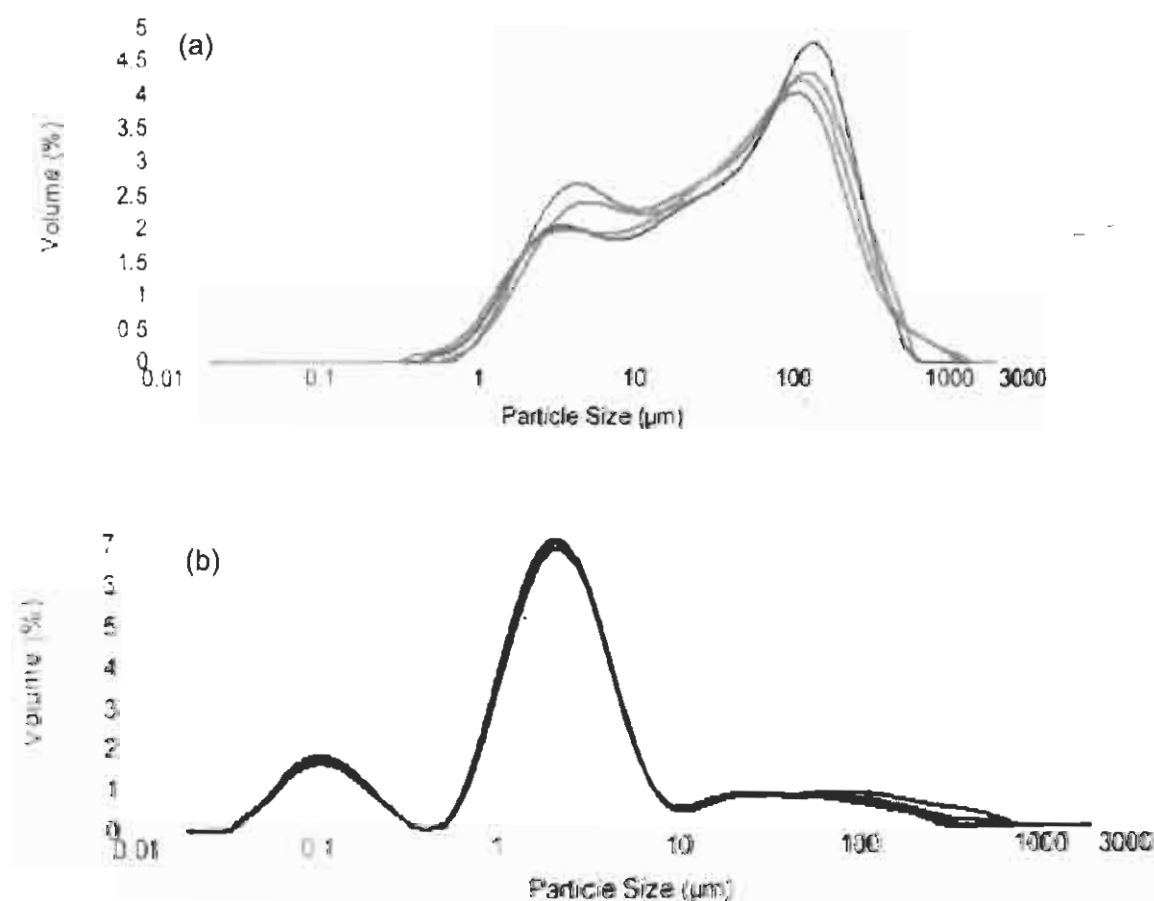


Figure 4.6. Particle size distribution volume percentage as a function of particle size for (a) uncleaned nickel particles and (b) cleaned particles

4.2.5.2. XRD and EDS

To confirm the presence of nickel both XRD (Figure 4.7) and EDS (Figure 4.8) were done. The twin peaks (52° and $61^\circ 2\theta$) shown by XRD correlate with reports of nickel XRD analysis utilizing Co K α radiation.¹² The presence of Ni is confirmed by the EDS results shown in Figure 4.8.

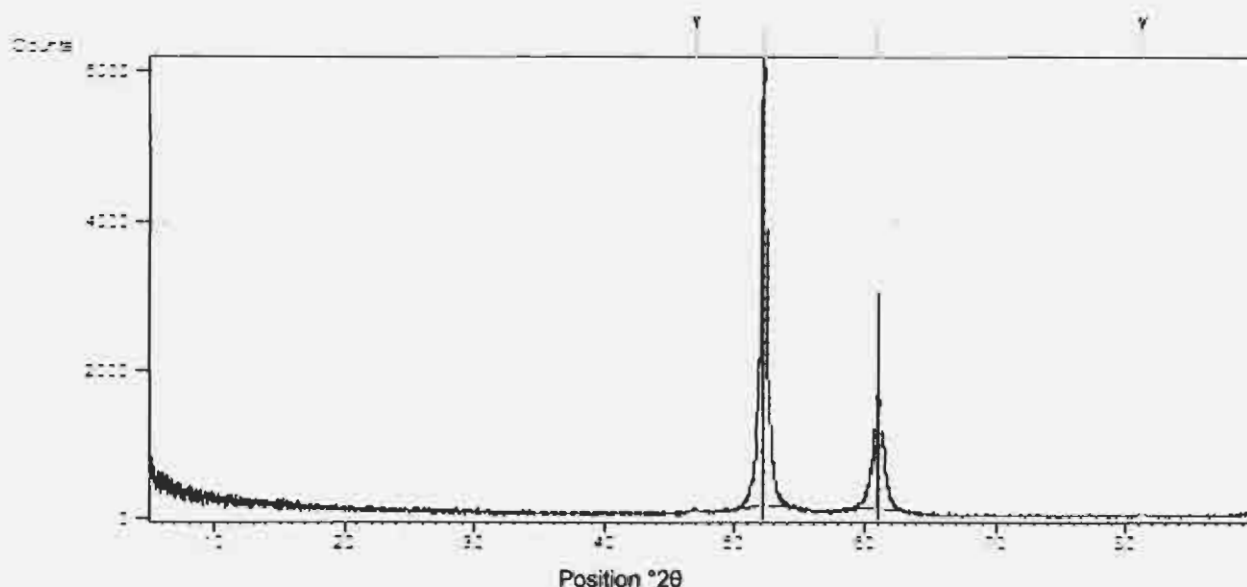


Figure 4.7. XRD of nickel powder prepared with 40 % (v/v) EtOH using Co K α radiation

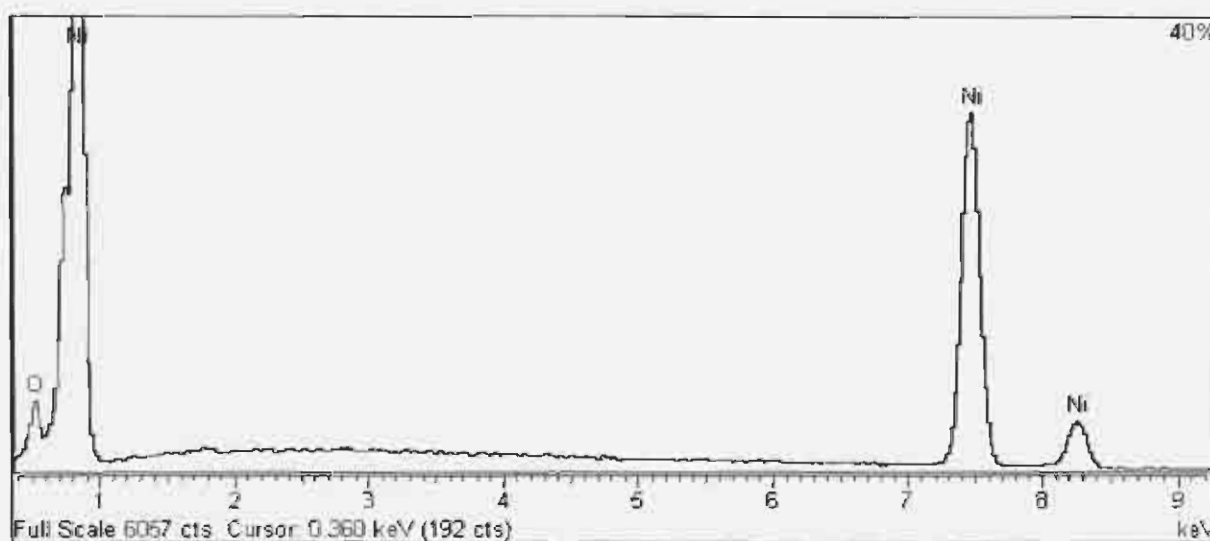


Figure 4.8. EDS analysis of nickel powder manufactured with 40% (v/v) EtOH

According to the XRD shown in Figure 4.7 only the two characteristic Ni peaks are present which means that the nickel particles analyzed are of adequate purity, confirmed by low levels of noise indicating small amounts of impurities. According to the specific XRD pattern the crystal structure is cubic.¹³ The EDS in Figure 4.8 confirms the purity of the Ni shown by XRD. The small amount of oxygen indicates that a small amount of nickel powder had been oxidized during preparation.

4.3. Dispersion formulation

The quality of the dispersion formulated for centrifugal dispositioning is important since the stability of the dispersion will determine the quality of the membranes produced. Dispersions are commonly stabilized using polymers.¹⁴ The three polymers that were evaluated in this study yielded various dispersion stabilities when dispersing the hydrothermally prepared nickel particles. It was shown that the polyacrylamide-co-diallyldimethylammoniumchloride (PAAco) performed better, i.e. yielded a higher dispersion stability than the two other polymers polyvinylpyrrolidone (PVP) and ammonium polymethacrylate (APMA).

The data given in Figure 4.9 depicts the stabilization of 0.01% to 0.25% (v/v) PAAco polymer as determined by measuring the light transmission (1100nm) of a dispersion over time. As the particles settle the transmission increases, i.e. the slower the transmission increases over time, the more effective is the polymer in stabilizing the dispersion. A control with only nickel particles (no polymer) in dispersion is given for comparison. Irrespective of the concentration, it can be seen that there was an increase in the stabilization of the nickel particles when compared to the control. An increase in the concentration of PAAco however had little significant effect on the stability of the dispersion. It seems that 0.025% (v/v) PAAco yielded the least stability, even less than 0.01% (v/v). While we are unable to explain this phenomenon, the same observation was made by Huyn *et al.* The reason why the transmission of the polymer does not reach a transmission of 100%, is because the very fine nickel particles remain dispersed when PAAco is present, irrespective of the amount of polymer used.

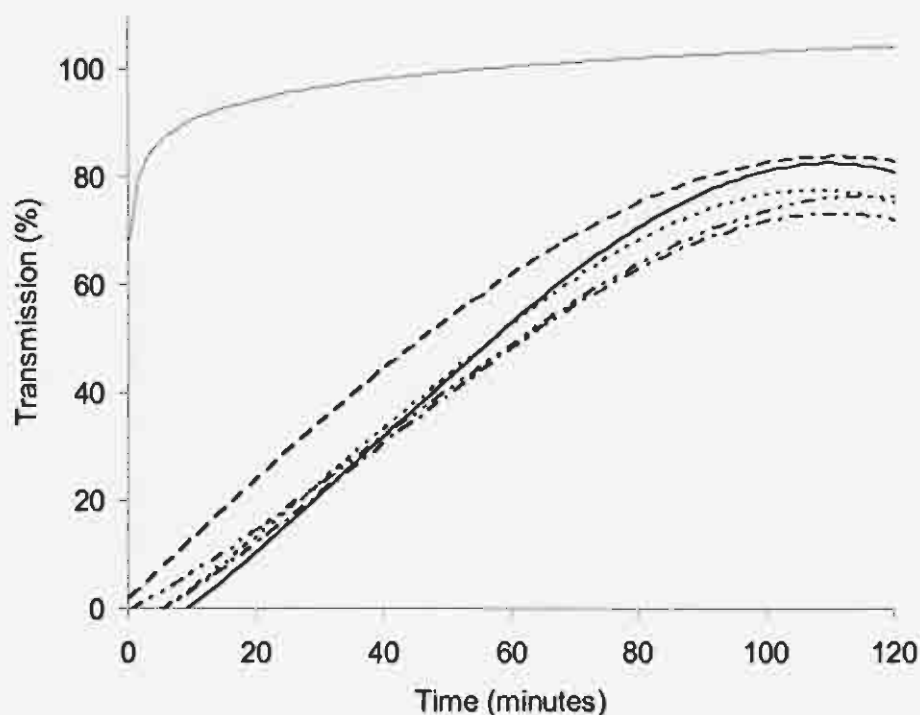


Figure 4.9. Percentage transmission as a function of time for polyacrylamide-co-diallyldimethyl ammonium chloride (PAAco) at concentrations 0.25%(v/v) (— · —), 0.1%(v/v) (— · —), 0.05(v/v) (·····), 0.025%(v/v) (— —), 0.01%(v/v) (—) and control (—)

Figure 4.10 shows the stability of the nickel particles in 0.01% to 0.25% (v/v) APMA as a function of time. When the various concentrations are compared to each other, it seems that an increase in the concentration of AMPA caused a gain in the dispersivity and stabilization for the nickel particles. The gain is however only significantly realized at concentrations of 0.1% (v/v) and above. When the various concentrations are compared to the control it can clearly be seen that all the concentrations offered an increase in the stability of the dispersion, but when the concentration increased to 0.1% (v/v) and above, the APMA showed a noticeable gain in dispersivity of nickel particles compared to lower concentrations. A gain of about 10 minutes (rate of breakage) is realized from the lowest to the highest concentrations. When the rate of breakage of PAAco and APMA is compared it was observed that PAAco had a substantially lower rate of breakage. However, the amount of breakage for the % transmission once equilibrium has been achieved (levelled of) is comparable for PAAco and APMA.

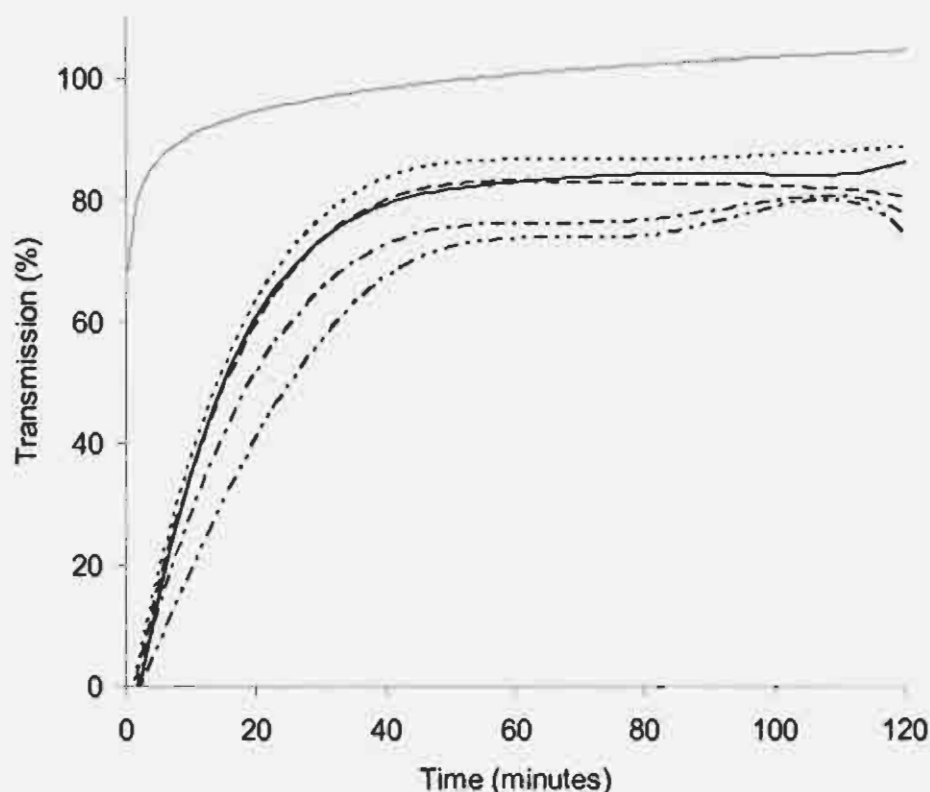


Figure 4.10. Percentage transmission as a function of time for ammonium polymethacrylate (APMA) at concentrations 0.25%(v/v) (— · —), 0.1%(v/v) (— · —), 0.05(v/v) (· · · · ·), 0.025%(v/v) (— —), 0.01%(v/v) (—) and control (—)

The results of the stabilization of nickel powders by PVP are given in Figure 4.11. When comparing the stability of all the concentrations of PVP to the control, it can be assumed that little stabilization occurred with an increase in the concentration of PVP, in terms of the rate of dispersion breakage. It seems however that the amount of breakage is concentration dependant. Interestingly enough more breakage (>90%) occurs at concentrations above 0.1% (v/v). Below 0.1% (v/v) transmission of 80% is achieved irrespective of the concentration. This increased breakage at higher polymer concentration could be due to agglomeration of the polymers themselves encapsulating the remaining Ni particles while becoming large enough in size to precipitate out of the dispersion causing the increase in breakage.

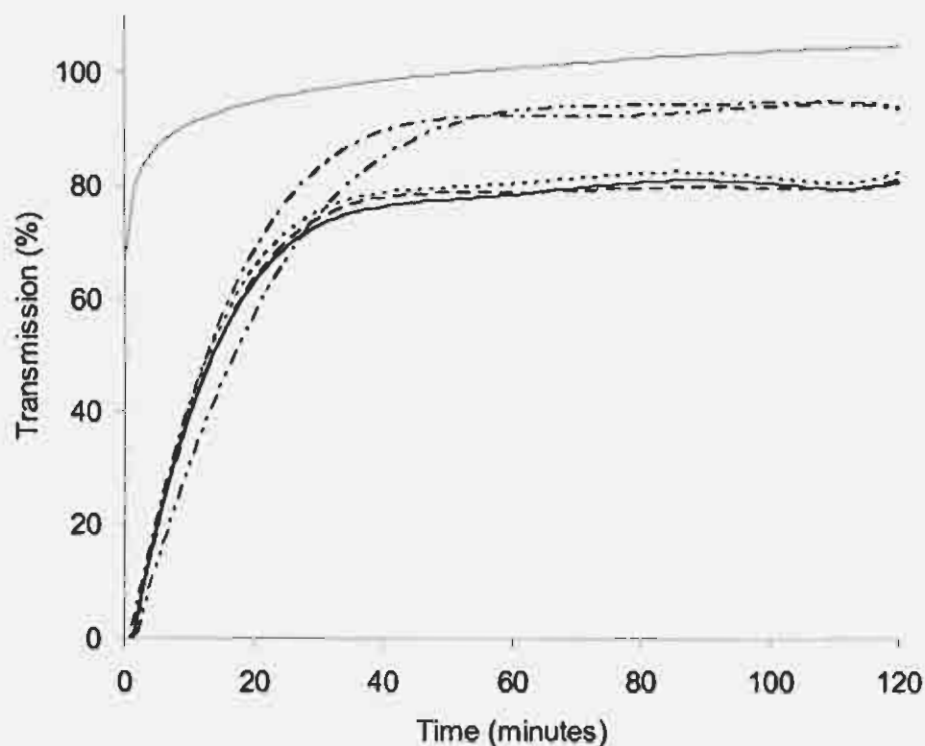


Figure 4.11. Percentage transmission as a function of time for polyvinylpyrrolidone (PVP) at concentrations at concentrations 0.25%(v/v) (— · —), 0.1%(v/v) (— · —), 0.05(v/v) (····), 0.025%(v/v) (— —), 0.01%(v/v) (—) and control (—)

When the effect of concentration on dispersion stability is compared for of PAAco, APMA and PVP, it is clear that PAAco didn't show a significant gain in dispersion stability, as opposed by APMA and PVP which indicated gains in dispersivity (the rate and amount of breakage in the case of APMA and the amount of breakage in the case of PVP) of the nickel particles with increasing concentration. According to Huyn *et al*¹⁵ acrylamide polymers possess the best stabilizing properties when compared to other polymeric dispersants. This is confirmed by Figure 4.12 and 4.13 where the efficacy of the three polymers is compared at 0.01% and 0.25% (v/v) respectively. At lower polymer concentrations (Figure 4.12) APMA and PVP showed little difference in the dispersion stabilization ability opposed to PAAco which showed a significant gain in dispersivity stabilization. For all three polymers the amount of breakage after 120 minutes was similar ($\pm 80\%$) although it does seem as if the PAAco might actually break further than APMA and PVP if the

experiments were done beyond 120 minutes. This was however not done since it was the sole aim to improve on stability for centrifugal dispositioning only.

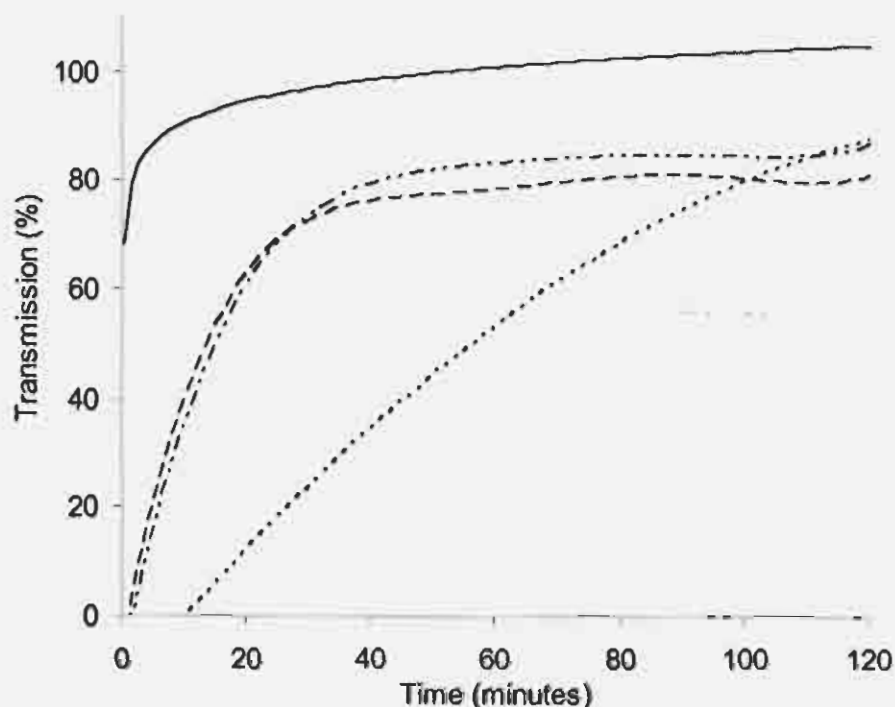


Figure 4.12. Percentage transmission as a function of time for PAAco, APMA and PVP at 0.01%(v/v) with PAAco (.....), AMPA (— —), PVP (— · —) and control (——)

At higher concentrations (Figure 4.13), the stabilization ability of APMA and PVP is improved because of the increase in their concentrations. PAAco however showed little gain in stabilization of the nickel particles when compared to the results in Figure 4.12. PVP displayed the least increase in stability of the nickel particles while APMA showed a noteworthy increase in dispersion stability at higher concentrations. It can thus be assumed that APMA and PVP proved to be sensitive to fluctuations in the polymer concentration while PAAco indicated more or less the same dispersivity, irrespective of concentration, i.e. PAAco is as effective at low concentrations as it is at higher concentrations. While the rate of breakage decreased for APMA and PVP with increasing time, the amount of breakage was higher for PVP at higher concentrations as already observed when discussing Figure 4.11. Contrary for APMA, the amount of breakage decreased slightly with

increasing concentration to a transmission of approximately 70% which was very similar than the amount of breakage observed for PAAco.

When comparing Figures 4.12 and 4.13 it can be seen that PAAco provided more stabilization for the nickel particles when compared to APMA and PVP, irrespective of the concentration used. This is confirmed by literature which explains the higher stability of nickel powders with polyacrylamides because of the adsorption affinity of polyacrylamides for nickel which is higher than for Ni than the affinity displayed by APMA or PVP.¹⁵

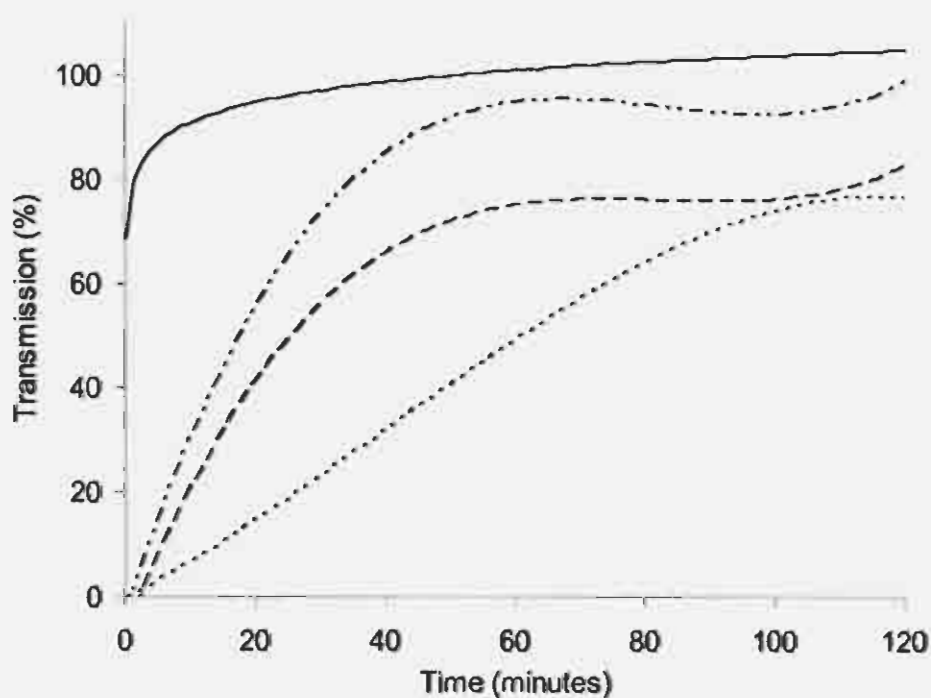


Figure 4.13. Percentage transmission as a function of time for PAAco, APMA and PVP at 0.25%(v/v) with PAAco (····), APMA (— —), PVP (— · —) and control (—)

4.4. Centrifugal Positioning

After the nickel powders were formulated into a dispersion with PAAco (0.5% (v/v)), the dispersion was placed into the stainless steel mould of the custom built centrifuge. The dispersion was sealed off by plastic plugs on both sides and the dispersion centrifuged around its longitudinal axis at 12000 rpm for 10 minutes. Afterwards, the plugs were removed and the membrane left to dry in the mould, before it was removed. During this process several problems occurred.

The first problem related to the wax-coating used on the inner side of the mould, which is used to prevent the membrane from sticking to the inner surface of the mould after centrifugation by promoting easy removal. The wax-coating is applied by dipping the mould in petroleum jelly dissolved in petroleum ether. After evaporation a thin layer of petroleum jelly remains on the inner mould surface. It was found that the removal of the membrane was only possible when the mould was immersed in the petroleum ether solution twice. However, when coating the mould surface more than twice the application procedure yielded a decrease in the removability of the membrane from the mould due to the adhesance of the nickel membrane to the inner mould surface. More coatings resulted in a larger amount of wax-coating being applied to the inner mould surface, and as a result more petroleum jelly that migrates when the temperature inside the mould increases as a result of the heat developed by the centrifugal process. This increased impregnation of petroleum jelly caused the membranes to crack during the drying period in the mould.

Another problem related to the speed of centrifugation. The speed at which the nickel membranes were centrifuged had to be decreased from 17000rpm, which is the speed usually employed when α -alumina dispersions are centrifuged, to 12000rpm for the nickel dispersions. This was done in another attempt to decrease membrane cracking after centrifugation. Since the density of nickel is 8.9 g.cm^{-3} and α -alumina's is 3.99 g.cm^{-3} , it can be assumed that the centripetal forces of the nickel particles will be higher when compared to the centripetal forces of α -alumina particles, which will affect the packing density of the greencasted membrane, i.e. less force should give similar densities (packing) when using Ni powder instead of α -alumina powder.

Apart from the petroleum jelly, the main cause of membrane cracking was due to contaminants present in the greencasted membrane. There are various ways in which these contaminants could have gained access to the nickel membrane and include:

- Inadequate cleaning of the stainless steel mould and plastic plugs.
- Contaminants in the petroleum ether/petroleum jelly solution because of exposure to the atmosphere.
- Contaminants in the nickel/PAAco dispersion because of (1) exposure to the atmosphere, (2) chemical and magnetic agglomeration of nickel particles for example due to the residual presence of Na-CMC.

The mould and plugs used in the centrifugation posed problems and increased membrane cracking, especially when residual α -alumina or nickel particles remained on these surfaces after a previous centrifugation. To combat this, the mould and plugs were washed and cleaned with dishwashing liquid prior to every centrifugation. The wax-coating applied by means of the petroleum ether/petroleum jelly solution caused the membranes to crack if the solution was left open, allowing the solution to collect dust from the atmosphere. Contamination by dust also occurred with the nickel powders (whether or not in dispersion) when left open and hence exposed to the atmosphere. The nickel powders, after cleaning, were thus kept in air tight containers until it was dispersed or centrifuged.

The biggest problem however occurred due to chemical and magnetic powder agglomeration. Initial powders that weren't washed appropriately or that were prepared on a magnetic stirrer produced the agglomerates described in Section 4.2.4 and 4.2.5.1. After reducing the agglomerates to a minimum using washing and grinding and adhering to all the modifications described above it was finally possible to produce a centrifugally dispositioned Ni greencast without any defects.

The drying procedure in the cast after centrifugation had to be carried out in a temperature controlled environment. Temperature fluctuations during night and day caused the membrane to shrink and expand resulting in cracking of the membrane. By drying the membrane in an oven at 30°C, further cracking was eliminated.

It is clear from the previous discussion that there are several factors that can contribute to the cracking of nickel membranes during and after centrifugation, i.e. prior to sintering. All these problems were however successfully overcome with small alterations in the membrane preparation procedure. Since centrifugal dispositioning is an important membrane manufacturing step in this study, special care had to be taken to ensure the optimal formation of the membrane. Photographs of a nickel membrane after centrifugation in the mould is shown in Figure 4.14.



Figure 4.14. Nickel membranes produced by centrifugal dispositioning directly after centrifugation in the stainless steel moulds

4.5. Sintering

After the nickel membranes were dispersed, centrifuged and removed from the stainless steel moulds without cracking, they could finally be sintered using a specific sintering programme. The programme is designed to gradually increase the heating rate as described in Section 3.5, which is again done to prevent the membrane from cracking. A heating rate above $1.2^{\circ}\text{C}\cdot\text{min}^{-1}$ lead to membrane cracking and collapsing due to the rapid expansion of the nickel. When a controlled heating rate below $1.2^{\circ}\text{C}\cdot\text{min}^{-1}$ was used, no membrane cracking or rupturing occurred. The nickel membrane oxidized during the sintering experiments to green nickel(II)oxide (bunsenite) as shown in Figure 4.14.

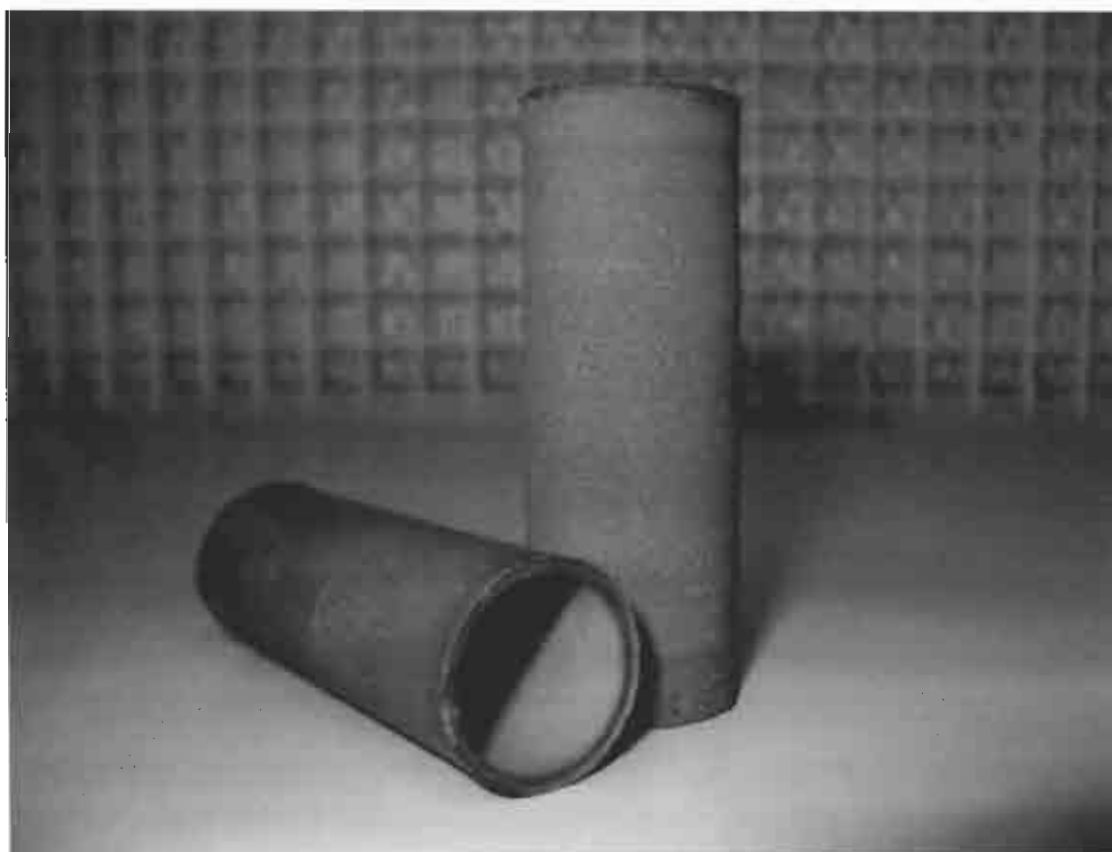


Figure 4.14. Sintered asymmetrical porous nickel membrane

4.6. Membrane Characterization

4.6.1. Dimensions and shrinkage

In Table 4.2 the change in dimensions of the nickel membranes with increasing sintering temperatures is presented and expressed in terms of the inner, outer and length dimensions of the nickel membranes. The % inner, outer and length shrinkage in terms of the greencast is presented in Figures 4.15, 4.16 and 4.17 respectively.

Table 4.2. Outer, inner and length shrinkage of porous nickel membranes sintered at various temperatures

Sintering temperature (°C)	Length (mm)	$\varnothing_{\text{inner}}$ (mm)	$\varnothing_{\text{Outer}}$ (mm)
Greencast	58.66	18.02	20.44
950	54.16	17.10	18.68
1000	52.26	17.00	18.58
1050	53.40	16.40	18.32
1100	52.10	16.00	18.40
1150	51.68	16.28	18.32
1200	51.14	16.10	18.06
1250	50.64	16.30	17.80

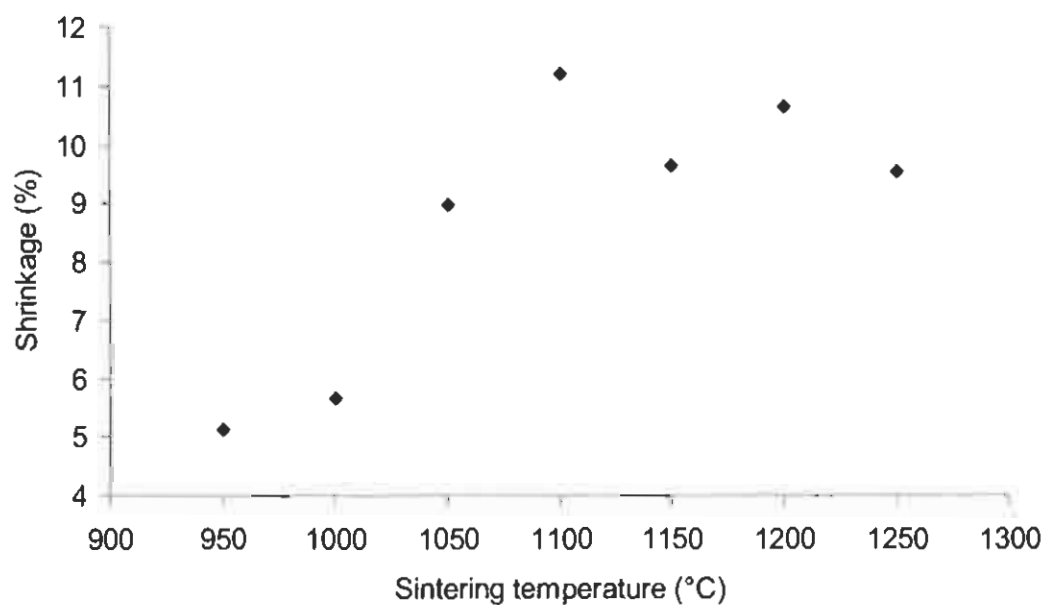


Figure 4.15. Shrinkage of the inner diameter of nickel membranes as a function of sintering temperature

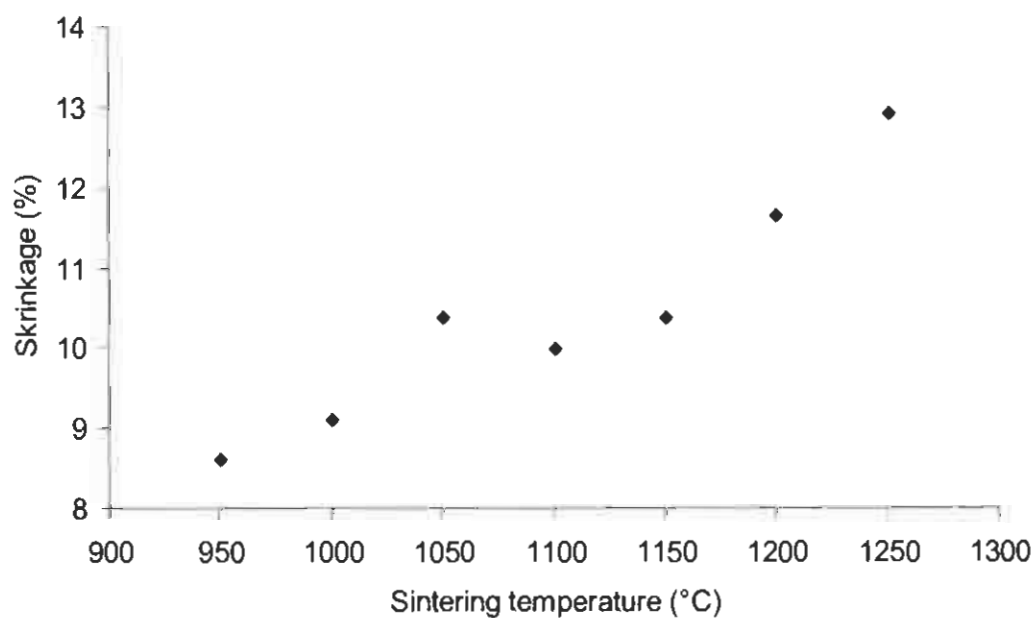


Figure 4.16. Shrinkage of the outer diameter of nickel membrane as a function of sintering temperature

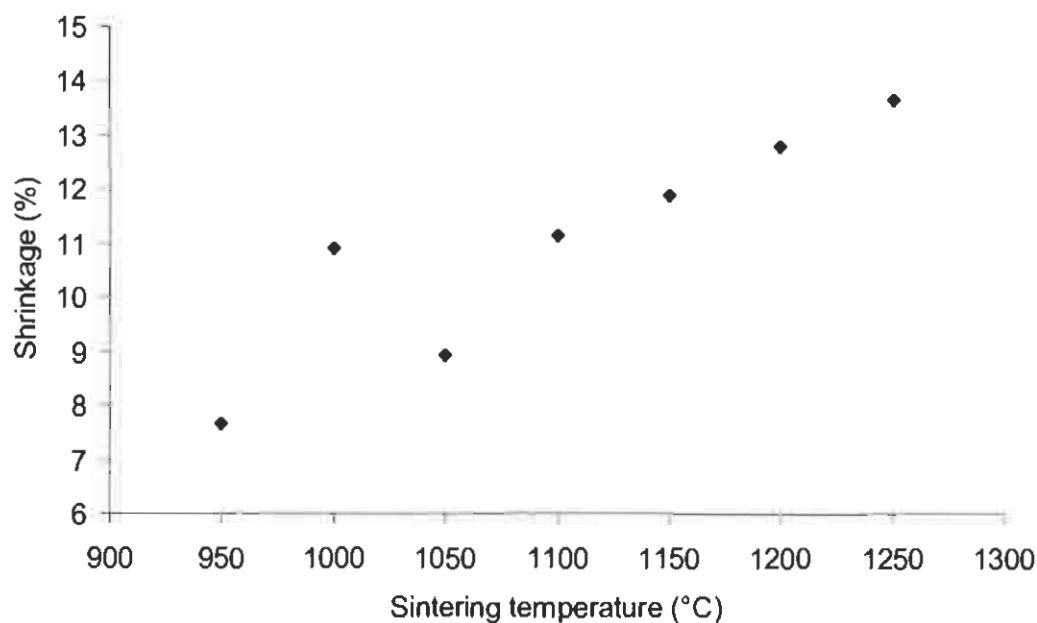


Figure 4.17. Shrinkage of the length of the nickel membrane as a function of sintering temperature

From Figure 4.15 it can be seen that the axial shrinkage of the inner diameter showed an initial increase in shrinkage with increasing sintering temperature from 950°C to 1050°C, where after the shrinkage remained approximately constant. However, according to Figure 4.16 the shrinkage of the outer diameter increased linear over the whole sintering range. Thus when comparing Figure 4.15 and Figure 4.16 it becomes clear that while linear shrinkage can be observed for the outer diameter over the whole temperature range, the increase in shrinkage ceased at 1050°C for the inner diameter. A possible explanation for this could be that the packing of particles on the inside of the membrane is denser than the packing density on the outer side of the membrane, due to the presence of the smaller particles on the inside. This implies that the inside densified faster reaching a maximum at 1100°C.

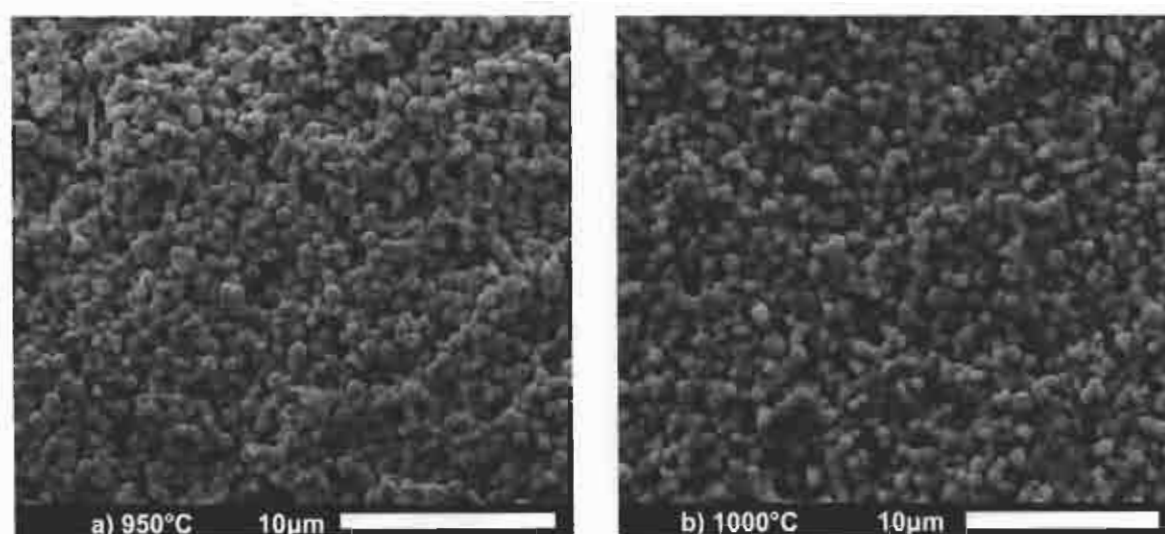
The linear shrinkage depicts the shrinkage over the length of the membrane. According to Figure 4.17, the linear shrinkage increased linearly with sintering temperature over the whole range of sintering temperatures, which correlates with the outer axial shrinkage.

The shrinkage due to the drying of the greencast was also measured. This was done by comparing the dimensions of the membrane in the mould directly after centrifugation with a dried membrane just before sintering. The mould measured 80.44 mm and since the plastic plugs were 10.01 mm, the membrane should be 60.42 mm in length. The inner diameter of the mould was 21.24 mm. By comparing the experimental dimensions of the dried greencast (Table 4.2) with the theoretical dimensions of the greencast directly after centrifugation, it was observed that the greencast had a length of 58.66 mm and an outer diameter of 20.44 mm. This corresponds to a drying percentage shrinkage of 2.91% for the length and 3.77% for the outer diameter of the membrane.

The trends observed in Figures 4.15 to 4.17 correlate to the findings of Bissett , Steenkamp *et al* and Zah *et al* where the observed linear shrinkage was ascribed to densification of the membrane mainly due to grain growth, and surface diffusion and other sintering mechanisms.

4.6.2. SEM

SEM photographs showing the inner surface and inner and outer cross-sections of the nickel oxide membranes as a function of sintering temperatures are shown in Figures 4.18 and 4.19 respectively.



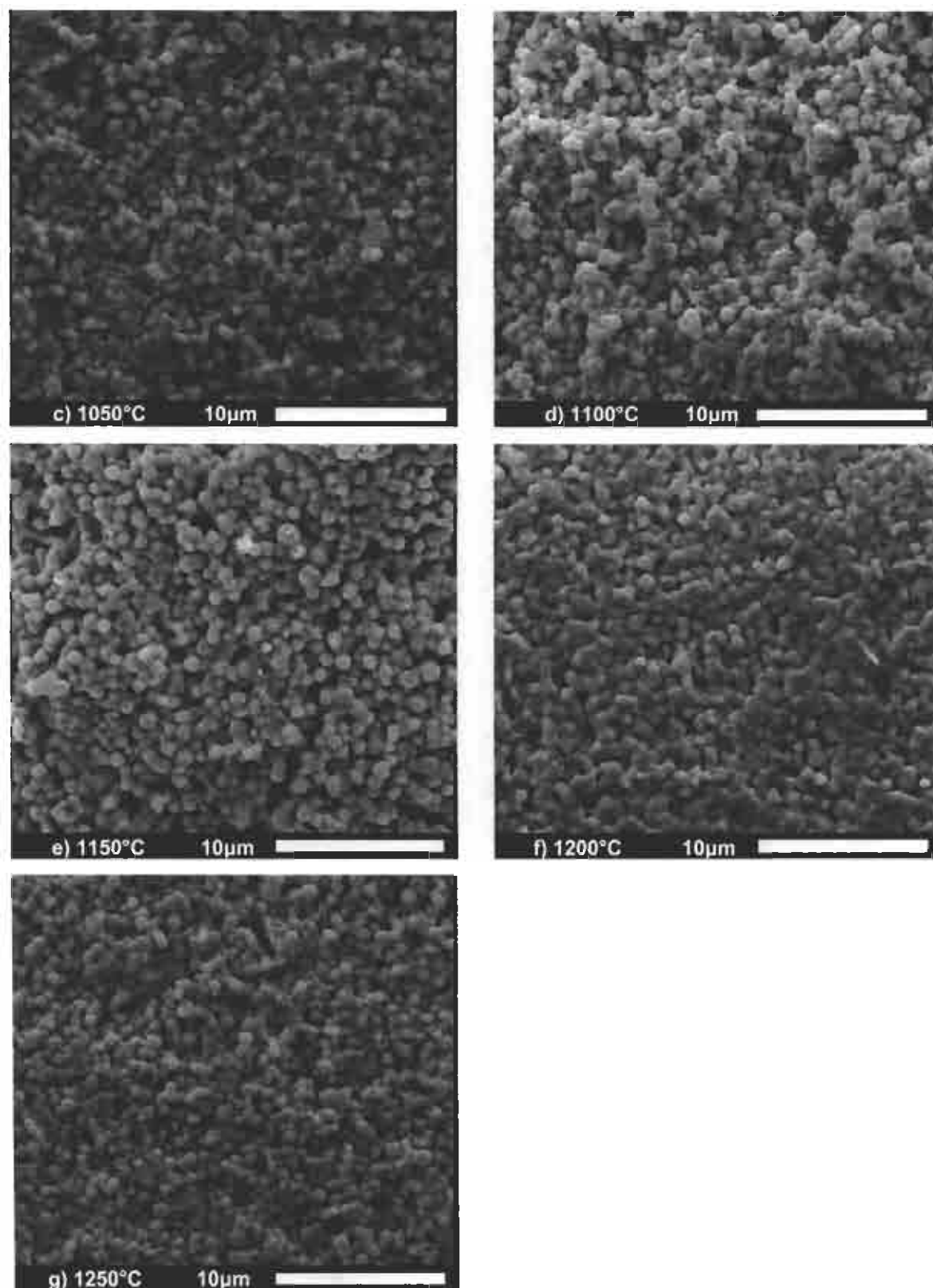


Figure 4.18. SEM photographs of the nickel oxide membranes' inner surface sintered at (a) 950°C, (b) 1000°C, (c) 1050°C, (d) 1100°C, (e) 1150°C, (f) 1200°C and (g) 1250°C

According to the SEM photographs in Figure 4.18, a significant change in the inner surface of the nickel membrane could not be observed with the exception of Figure 4.18 (F). A trend could however not be confirmed as the morphology remained the same from 1200°C (F) to 1250°C (G). This lack of change could however be to the close packing of the particles on the inside surface of the membrane, and might therefore not be representative of the complete membrane. This was found to be the case when studying the cross section as a function of the sintering temperature. (Figure 4.19)

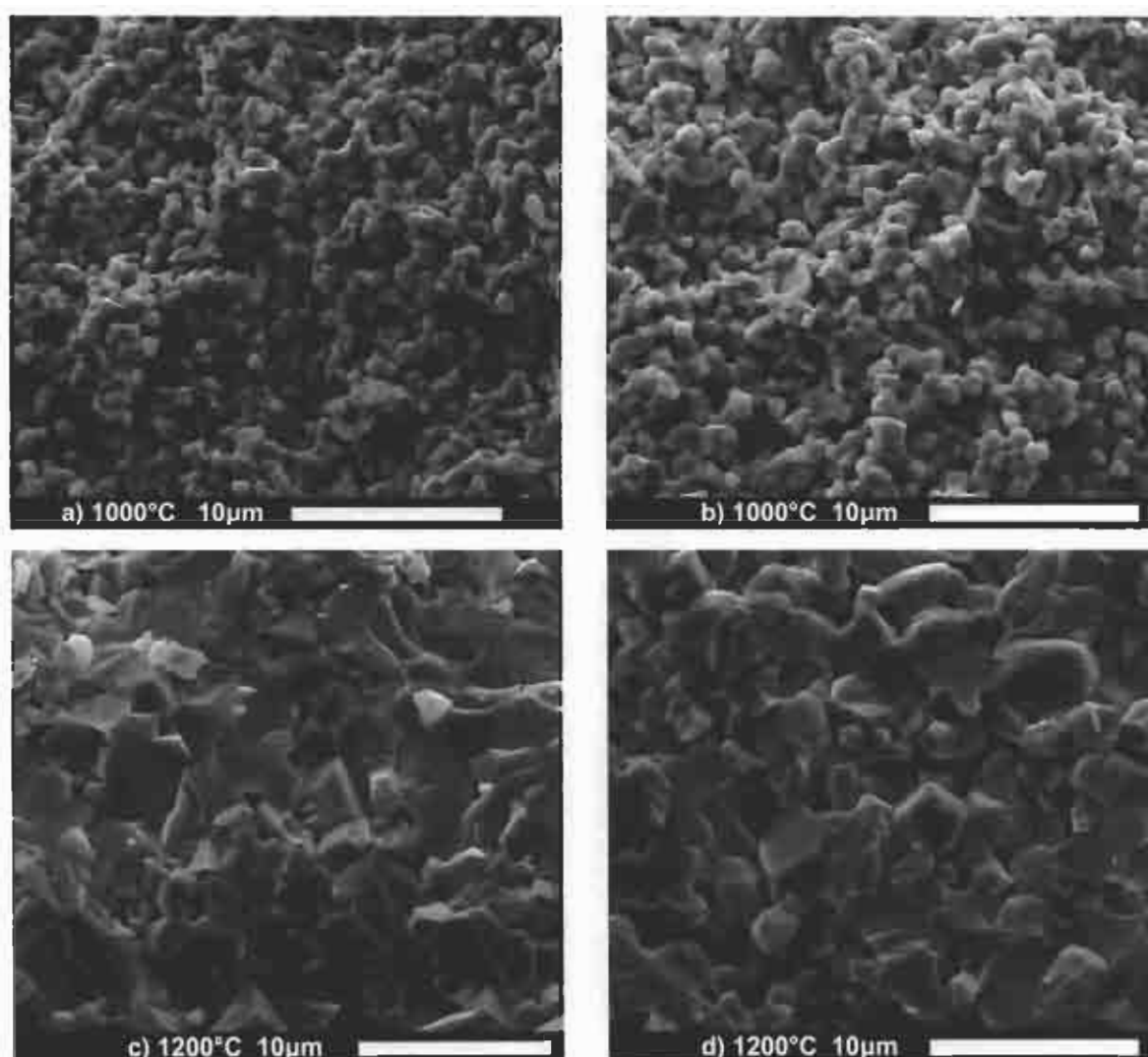


Figure 4.19. SEM photographs of the inner (a, c) and outer (b, d) cross section of the nickel oxide membranes sintered at (a, b) 1000°C and (c, d) 1200°C

The SEM photographs of the cross-sections of the membrane (Figure 4.18) provide deeper insight to the changes involved in the membrane morphology with increasing sintering temperature. It can be seen that when comparing the inner and outer cross sections at 1000°C (Figures 4.19 (a) and (b)) to the inner and outer cross section at 1200°C (Figures 4.19 (c) and (d)) a clear change in the morphology of the membrane particles has occurred. The reasons for the change can be explained by the chemical properties of nickel and nickel oxide at high temperatures. Bobrovskii *et al*¹⁶ reported that an alteration in the lattice parameters of nickel oxide occurred at temperatures of 1200°C and above. This leads to an increase in the thermal expansion coefficient associated with the presence of magnetic transformation which explains the significant increase of the crystal size from 1000°C to 1200°C.

4.6.3. Mercury porosimetry

The results obtained from the mercury porosimetry analysis are given in Figures 4.20-22. Due to the shift in the thermal expansion coefficient of nickel oxide at temperatures of 1200°C and above, irregular values in the porosity and pore diameter were observed.

The porosity of nickel oxide membranes as a function of sintering temperature is given in Figure 4.20. According to the graph the porosity decreased exponentially with increasing sintering temperature correlating to the increase in shrinkage discussed previously. The sharp decrease in the porosity at sintering temperatures above 1150°C can be explained by the positive shift in the thermal expansion coefficient. This means that the nickel oxide will expand faster above 1200°C causing the porosity to rapidly decrease with a small change in temperature. This is in contrast to the α -alumina membranes which displayed a linear decrease of porosity with an increase in sintering temperature.¹⁷

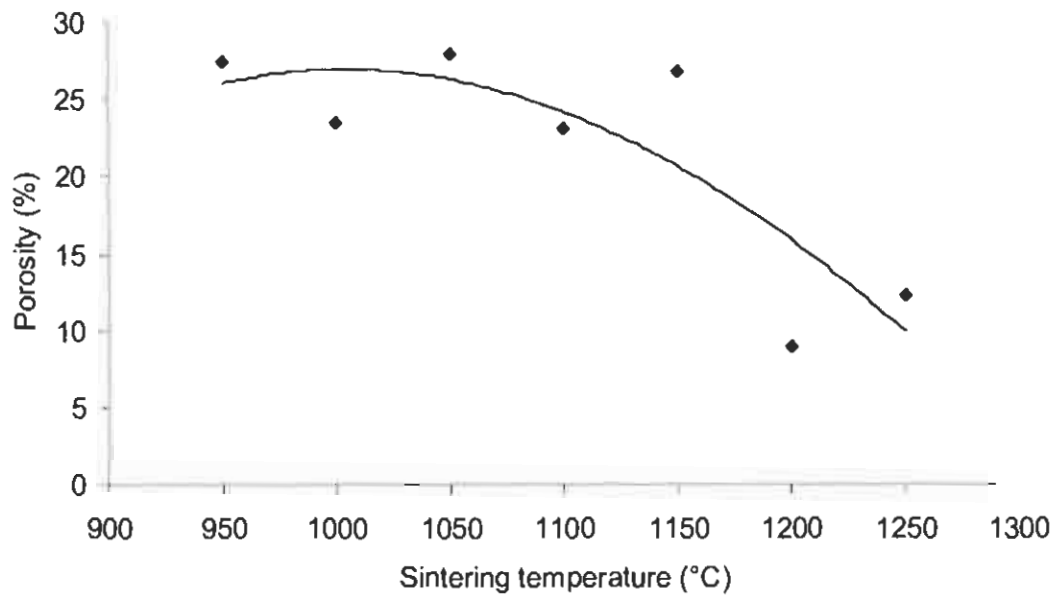


Figure 4.20. Porosity as a function of sintering temperature

In Figure 4.21 a graph is shown where the average pore size is plotted a function of sintering temperature. According to Figure 4.21, an increase in the sintering temperature did not lead to a significant change in the average pore diameter which remained approximately $0.4 \mu\text{m}$. This could mean that 6 nickel oxide particles surround a pore, since it has been shown that in such a case the pore size remains constant with an increase in sintering temperature.¹⁸ By utilizing Pythagoras' theorem, the theoretical average pore size can be calculated as follows:

$$\begin{aligned}
 (r + r_h)^2 &= 2r^2 \\
 r + r_h &= \sqrt{2}r \\
 r_h &= (\sqrt{2} - 1)r \\
 r_h &= 0.414r
 \end{aligned}$$

where r is the radius of the NiO particle and r_h is the radius of a sphere inside the pore. At 40% ethanol, the average particle size (r) is approximately $1 \mu\text{m}$ (Figure 4.4) and the average pore size (r_h) $0.4 \mu\text{m}$ (Figure 4.21). This clearly shows that experimentally $r_h = 0.4r$ which correlates with the mathematical calculation. Since the mathematical calculation is based on the approximation of 6

particles surrounding a pore, it does confirm the theory of negligible reduction of pore size with increasing sintering temperature if the pores on average are surrounded by 6 particles.¹⁹

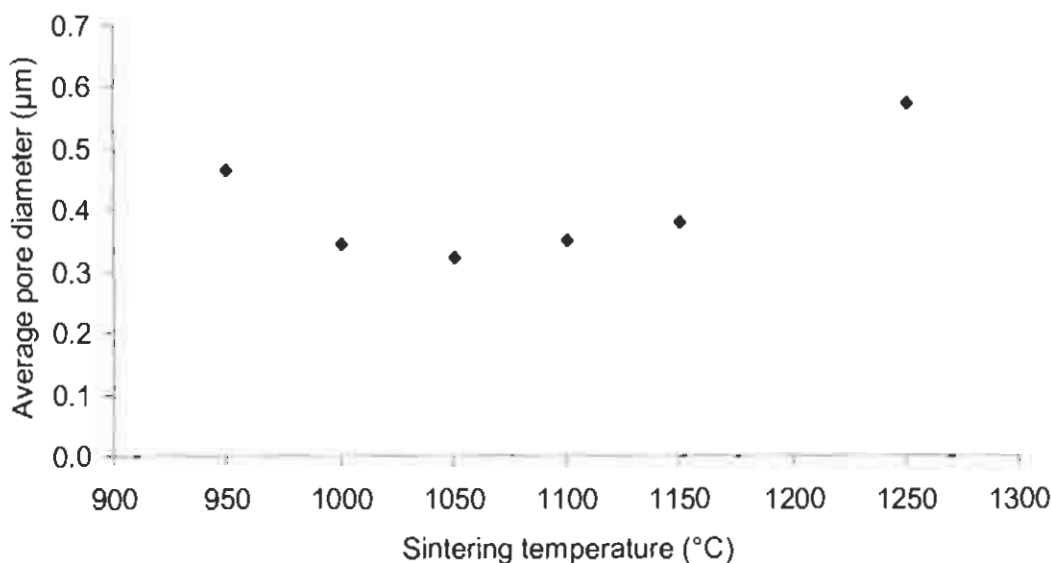


Figure 4.21. Average pore diameter as a function of sintering temperature

Kim *et al*²⁰ found that the pore size when using two different particle sizes (0.5 μm and 0.8 μm) in α-alumina membranes remained constant with increasing sintering temperature. This seems to confirm that the porosity may be more dependent on the sintering temperature, while the pore size may be more dependent on the size of the initial powder. The repeatable sharp increase in the pore diameter at 1200°C can only be ascribed to the change in crystal structure of nickel oxide.¹⁶ It is however not certain why this transition caused such a significant increase in average pore size which was only observed at 1200°C, i.e. not at 1150°C and not at 1250°C.

Finally, the pore volume as function of pore diameter at different is given in Figure 4.22. At 950°C (—), a bimodal distribution is apparent. According to the two peaks, there is a narrow pore size distribution around 0.3 μm and a wide distribution around 0.45 μm. The membrane sintered at 1100°C (— —) still has a bimodal pore size distribution, but in this case the fraction of small pores has substantially increased at the cost of the larger pore fraction. That means that although the average pore size has approximately remained constant (Figure 4.21), there has been a shift towards smaller pores as was expected in view of the shrinkage observed (Figure 4.15 - 4.17). This would also help explain why the small pore fraction average has increased from 0.3 μm to

approximately $0.35\mu\text{m}$. As the temperature increases further, the contribution of larger pores is decreasing further at the cost of the contribution of smaller pores. In fact, in the case of the membrane sintered at 1150°C , the bimodal pore size distribution has disappeared completely. Again there was a slight shift of the now combined pore size distribution to approximately $0.4\mu\text{m}$. The area of the 1150°C single peak has increased in terms of the width confirming that although it can now be described as a monomodal distribution, it includes a wide variation of pore sizes. This again confirms the shrinkage of larger pores and hence an increase in the amount of smaller pores. According to the theory of Chiang *et al*²¹ who have shown that pores surrounded by 6 or less particles shrink, it would imply that the large pores observed for the Ni membranes (approximately $0.45\mu\text{m} - 0.5\mu\text{m}$) have less than 6 particles surrounding it.

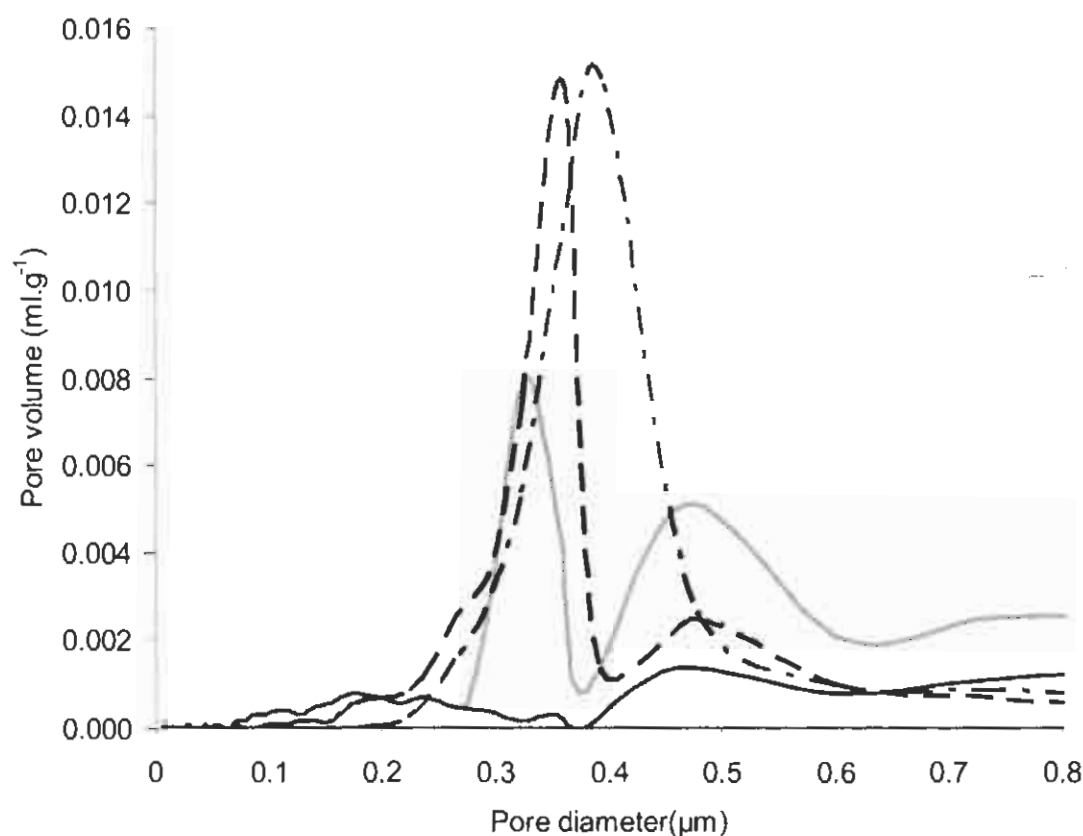


Figure 4.22. Pore volume as a function of pore diameter for sintered nickel oxide membranes at 950°C (—), 1100°C (---), 1150°C (-.-.), 1250°C (....)

At 1250°C, the phase transition has occurred, which is reflected in the pore size distribution shown in Figure 4.22. There seems to be very little correlation between the distributions before 1200°C and the distribution of 1250°C. At 1250°C there is again a bimodal distribution. However, the distribution for both peaks is very wide with average pore sizes just below 0.2µm and 0.45µm. The strong decrease in pore size (0.2µm) could result from the increase in particle size (see Figure 4.19) occurring at the cost of the pores. The decreased pore volume also correlates with the exponential decrease in porosity observed in Figure 4.20

4.6.4. Membrane strength

According to the strength test, the strongest nickel oxide membranes had a break strength of 507 MPa, and the weakest membrane had a strength of 67 MPa. Since the apparatus had been developed for much higher strengths, the error of the analysis was between 15% (1250°C) and 100% (950°C), which means that it is not possible to draw any conclusions from the change in strength as a function of sintering temperature. By comparing the strength of the nickel oxide membranes to the strength of α -alumina membranes produced by Bissett, it can however be seen that the nickel oxide membranes are 5 to 10 times weaker.

The Mohs hardness can be used to explain the weak membrane strength of the nickel oxide membranes. This test determines the ability of one material to scratch another. The material that is scratched by the other material is the weaker material and is arranged in lower order on the Mohs scale.²² The Mohs hardness for NiO is 5.5²³ and for α -alumina are 9.²⁴ This is probably the most important factor contributing to the weaker strength of the nickel membranes when compared to the α -alumina membranes. This means that the α -alumina is harder than NiO which could help explain the decreased strength of the NiO compared to the α -alumina.

4.6.5. Water permeance

Some of the membrane variables that influence the permeance of a liquid through a porous structure can be expressed in terms of the Hagen-Poiseuille equation.

$$J = \frac{\varepsilon r^2 \Delta P}{\tau 8\eta \Delta x} \quad (2.3)$$

Where J is the water flux through the membrane ($\text{mol.m}^{-2}.\text{s}^{-1}$ often expressed in terms of $\text{L.m}^{-2}.\text{h}^{-1}$), r is the pore radii (m), ε is the porosity (%), ΔP is the pressure difference over the membrane (Pa), Δx is the membrane thickness (m), τ is the tortuosity (-) and η the viscosity of water (0.001 Pa.s). For this study the water flux was experimentally determined for the membranes sintered at the different sintering temperatures as a function of pressure ranging from 2 to 10 bar (Figure 4.24).

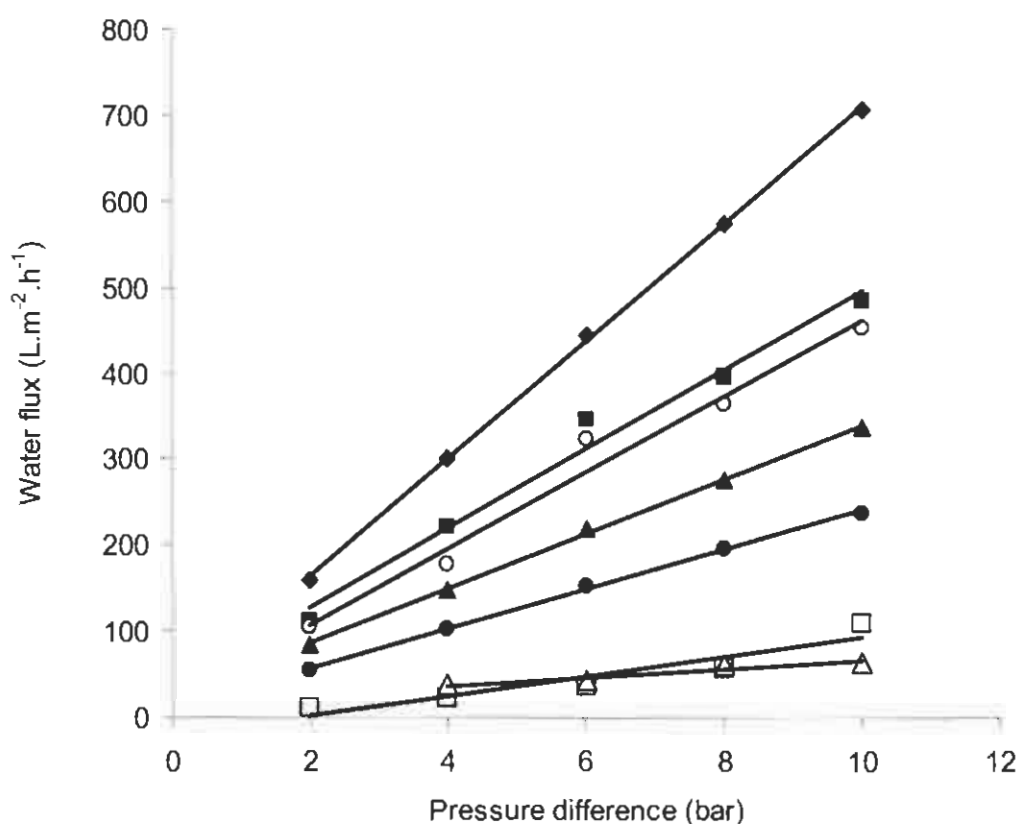


Figure 4.24. Volumetric flux of water through nickel oxide membranes sintered at 950°C (♦), 1000°C (■), 1050°C (○), 1100°C (▲), 1150°C (●), 1200°C (□) and 1250°C (Δ)

It can be seen from Figure 4.24 that there was a linear increase in water flux with increasing pressure difference across the membrane, for all sintering temperatures. This observation correlates with that found by Bissett and Steenkamp *et al*²⁵ for α -alumina sintered membranes. As the sintering temperature increased, the gradient of the corresponding graphs lines decreased, indicating a decrease in the permeance. From the gradient of the straight lines of Figure 4.24 the water permeance was calculated which is presented as a function of sintering temperature in Figure 4.25. According to the Hagen-Poiseuille equation the size of the pores and the porosity will have the most influence on the flux and hence permeance of membranes sintered at different temperatures since the other membrane parameters like the membrane thickness remain more or less constant. The tortuosity was taken as the reciprocal porosity and will hence not be elucidated separately. Since the average pore size for all of the membranes sintered below 1200°C remained relatively constant, the change in permeance could not be explained in terms of the average pore size.

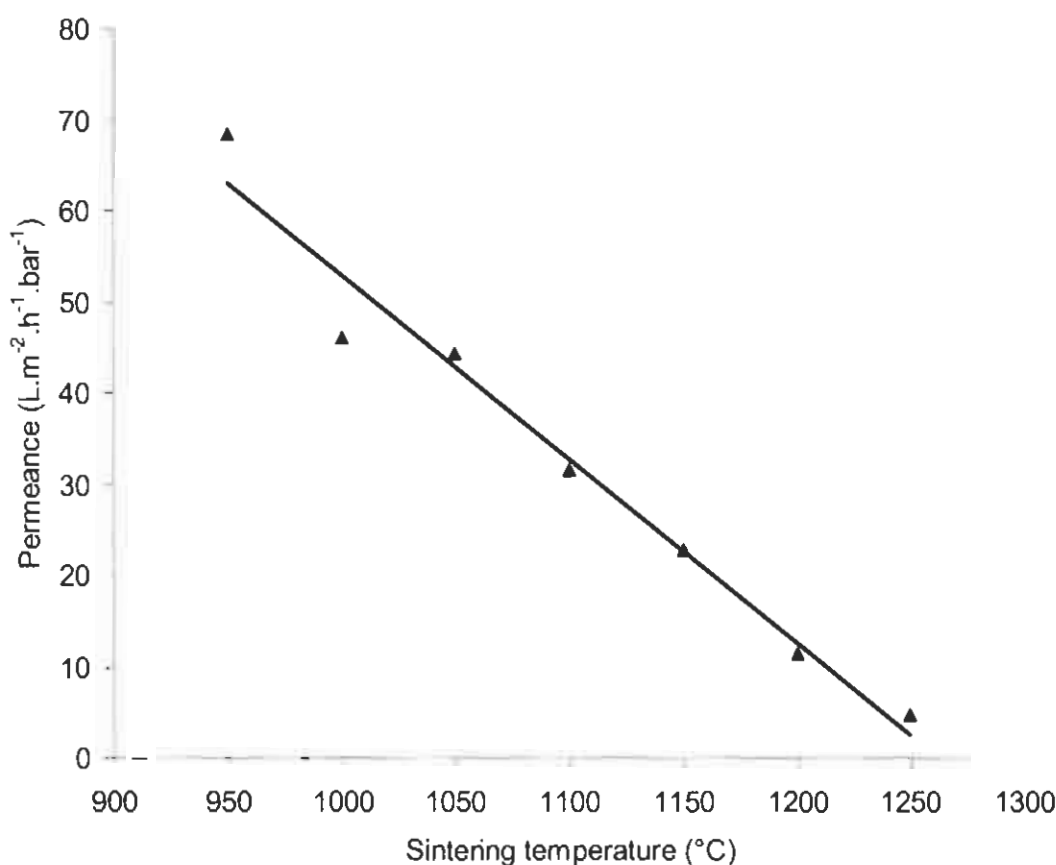


Figure 4.25. Water permeance as a function of sintering temperature

However, the data obtained from the porosity (Figure 4.20) in combination with the pore size distribution as indicated in Figure 4.22 may explain why the permeance decreases with increasing sintering temperature. The loss of a bimodal pore size distribution and the shifting of the peaks to the left indicate that larger pores are being exchanged for smaller pores as the sintering temperature increases. Because larger pores require lower pressures to penetrate, and higher pressures are needed to penetrate smaller pores, the decrease in flux can be explained for membranes made at sintering temperatures lower than 1150°C because of the increase in smaller pores. Additionally the decrease in flux at temperatures higher than 1150°C could be attributed to an increase in the amount of dead-end pores as sintering temperature increases, resulting in a decrease in flux. Furthermore it is accepted that the porosity is directly proportional to the flux (Equation 2.3) and hence understandable that the decrease in porosity (Figure 4.20) contributes to the decrease in flux and thus permeance.

It is clear that the nickel oxide membranes have a comparable (slightly improved) permeance when compared to alumina membranes made by the same manufacturing procedure (Table 4.3) when sintering temperatures of 1050°C was used to sinter the NiO membrane. It must be noted that the size of the particles to manufacture the membranes used by Steenkamp *et al* and Bissett, were comparatively smaller in comparison to the nickel particles used in this study.

Table 4.3. Water permeance comparison for various centrifugally dispositioned membranes sintered at 1050°C

Membrane	Permeance (L. m ⁻² .h ⁻¹ .bar ⁻¹)	Reference
AKP – 15*	41	Bissett ¹⁷
AKP – 15*	28	Steenkamp <i>et al</i>
Nickel oxide	44	This study

* Alumina particle size AKP -15 = 0.61µm manufactured by Sumitomo Chemical Corp, Osaka, Japan

When comparing the theoretical water permeance (using Equation 2.3) to the experimental water permeation (Figure 4.26) it seems that the initial theoretical water permeance was slightly lower than the experimental water permeation but nonetheless a reasonable good fit was obtained below 1100°C. At 1100°C however the theoretical water permeation equalled the experimental water permeation, followed by rapid an increase of the theoretical water permeation beyond the experimental water permeation when sintering temperatures reached 1200°C. To explain this, one has to consider the existence of dead-end pores that may exist when the sintering temperature reaches temperatures exceeding 1150°C. Furthermore, the Hagen-Poiseuille makes provision for the average pore size which was shown to increase drastically at 1200°C. Lastly, the equation does not make provision for bi- and monomodal distributions which, as has been shown previously, certainly contribute significantly to experimental water fluxes explained previously.

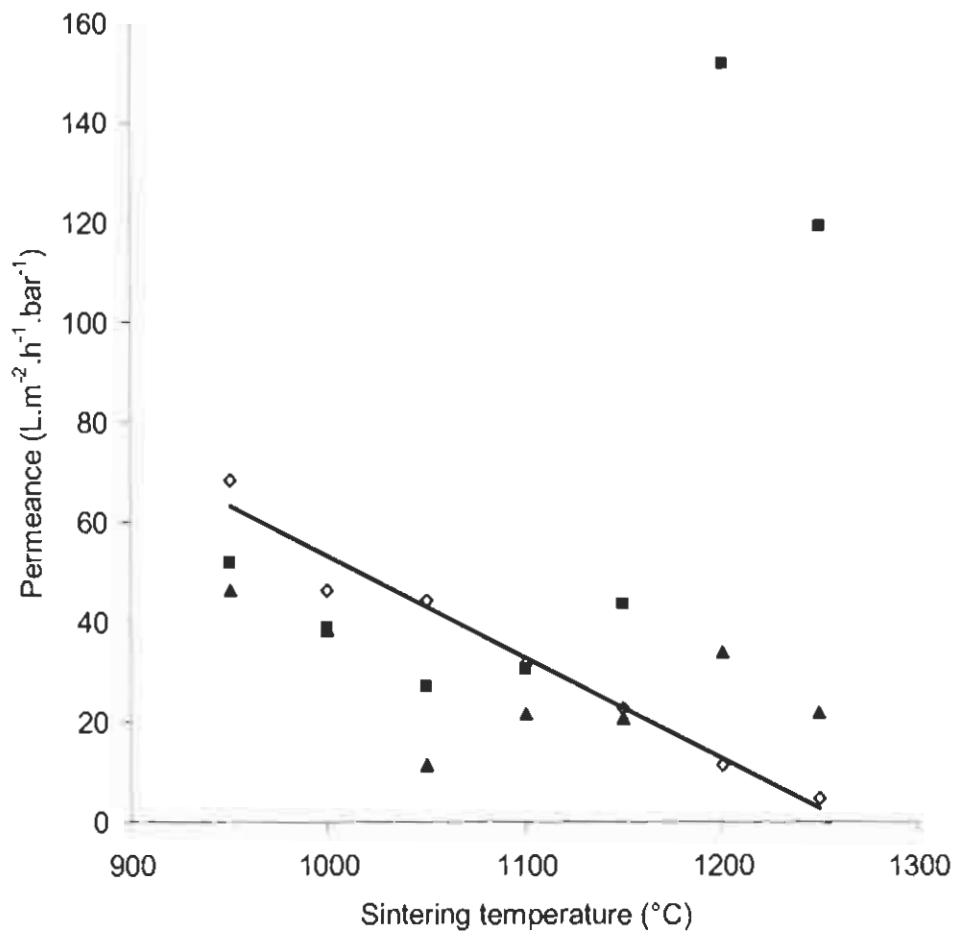


Figure 4.26. Comparison of the experimental water permeance (♦) to the theoretical water permeance using the average pore size (■) and to the theoretical water permeance using the cumulative pore size distribution (◇) as a function of sintering temperature

To demonstrate the influence of the pore size distribution on the theoretical flux, the Hagen-Poiseuille equation was used to calculate the theoretical flux at each individual point of the pore size distribution (see Figure 4.22) instead of using only the average pore size. This means that once the flux at each pore size has been calculated, it is added up over the whole pore size range. From the cumulative flux at each water permeation pressure, the theoretical permeance was calculated and plotted on the same graph (Figure 4.26) where the theoretical permeance calculations using the average pore size have been plotted. According to Figure 4.26, the cumulative permeance calculations gave a closer fit to the experimental permeance above 1150 °C. Although there is an increase in the theoretical cumulative permeance above the experimental permeance at 1200°C and above, the increase is much less than the permeance obtained when using the Hagen Poiseuille with the average pore size. This clearly shows that the cumulative calculation gives a closer fit and hence a better correlation for the experimental data when characterising the nickel membrane than the Hagen Poiseuille equation using the average pore size. This is understandable in view of the change in pore size distribution which is significant while the average pore sized remained nearly constant (except for the pore size at 1200 °C).

4.7. Conclusions

A porous nickel oxide membrane was successfully made by the centrifugal dispositioning technique. During the manufacturing and characterization experiments several observations and realizations were made. These include:

- The precipitation of the nickel particles produced particles that had a high Ni content after cleaning, had a uniform particle size distribution and were of a spherical shape. By varying the ethanol concentration the optimal particle size could be attained (40%).
- The PAAco polymer stabilized the Ni dispersion more effectively than APMA which in turn was more effective than PVP when tested in terms of the ability to disperse the nickel particles that had been produced by hydrothermal reduction.
- After a lengthy optimization process, it was shown that it is possible to manufacture a nickel green casted membrane repeatedly with centrifugal dispositioning without cracking during the drying period, and with easy removal from the mould. The membrane sintering produced uncracked nickel oxide membranes which had the following characteristics:
 - A constant average pore size and decreasing porosity with an increase in sintering temperature.
 - The porosity, pore size distribution, morphology, flux and permeance were all influenced by the change in the thermal expansion coefficient when sintering temperatures reached 1200°C.
 - The water permeation had a linear decrease with increasing sintering temperature because of the formation of dead-end pores and a shift in the pore size distribution resulting in the transition of larger pores to smaller pores.

- An increased brittleness when compared to α -alumina membranes produced by the same technique which can be attributed to the differences in the Mohs hardness of NiO and Al_2O_3 .

4.8. References

- ¹ A.Degen, J.Macek, Preparation of submicron nickel powders by the reduction from non-aqueous media, *Nanostructured materials*, **12**, 1999, 225
- ² D.H.Im, S.Y.Park, S.H.Huyn, B.Y.Lee, Y.H.Kim, Aqueous dispersion stability of nickel powders prepared by hydrothermal reduction method. *Journal of Materials Science*, **39**, 2004, 3629
- ³ J.Zah, H.M.Krieg, J.C.Breytenbach, Pervaporation and related properties of time-dependent growth layers of zeolite NaA on structured ceramic supports, *Journal of Membrane Science*, **284**, 2006, 276
- ⁴ <http://en.wikipedia.org/wiki/Nickel>
- ⁵ <http://aic.stanford.edu/sg/bpg/annual/v01/bp01-04.html>
- ⁶ K.H.Kim, H.C.Park, S.D.Lee, W.J.Wha, S.S.Hong, G.D.Lee, S.S.Park, Preparation of submicron nickel powders by microwave-assisted hydrothermal method, *Materials Chemistry and Physics*, **92**, 2005, 234
- ⁷ D.H. Chen, C.H.Hsieh, Synthesis of nickel nanoparticles in aqueous cationic surfactant solutions, *Journal of Materials Chemistry*, **12**, 2002, 2412
- ⁸ K. Tashiro, T. Watanabe, H.Inaba, H. Honma, Electroless nickel plating using hydrazine reducing agent with excellent bath stability, *Hyomen gijutsu*, **51**, 2000, 606
- ⁹ K.H.Kim, Y.B. Lee, E.Y.Choi, H.C.Park, S.S.Park, Synthesis of nickel powders from various aqueous media through chemical reduction method, *Materials Chemistry and Physics*, **86**, 2004, 420
- ¹⁰ K.H.Kim, Y.B.Lee, S.G.Lee, H.C.Park, S.S.Park, Preparation of fine nickel powders in aqueous solution under wet chemical process, *Materials Science and Engineering A*, **381**, 2004, 337

- ¹¹ K. Tashiro, S. Yamamoto, W.Daijyu, H. Honma, Smoothing of hydrazine reduced electroless nickel plating and its application for capping metal formation, *Hyomen gijutsu*, **53**, 2002, 71
- ¹² K.H.Lee, C.S.Jun, Preparation of palladium membranes for the reaction of $\text{Pd}(\text{C}_3\text{H}_3)(\text{C}_5\text{H}_5)$ with H_2 : wet impregnated deposition, *Journal of Membrane Science*, **157**, 1999, 107
- ¹³ <http://www.webelements.com/webelements/elements/text/Ni/index.html>
- ¹⁴ <http://www.en.wikipedia.org/wiki/polymers>
- ¹⁵ S.H.Huyn, D.H.Im, S.Y.Park, B.Y.Lee, Y.H.Kim, Aqueous dispersion stability of nickel powders prepared by a chemical reduction method, *Journal of Materials Science*, **39**, 2004, 3629
- ¹⁶ A.V.Bobrovskii, G.N.Kartmazov, V.A.Finkel, Crystal structure of nickel monoxide at high temperatures, *Izv. Akad. Nauk, USSR, Neorg. Mater*, **9(6)**, 1973, 1075
- ¹⁷ H.Bissett, Manufacture and optimization of tubular ceramic membrane supports, M.Sc dissertation, North West University, Potchefstroom, 2005, South Africa, Chapter 3: Ceramic support optimization, p 46
- ¹⁸ W.D.Kingery, H.K.Bowen, D.R.Uhlmann, Introduction to ceramics, 2nd Edition, Chapter 10, 1976
- ¹⁹ D.F.Shriver, P.W.Atkins, T.L.Overton, J.P.Rourke, M.T.Weller, F.A.Armstrong, Shriver & Atkins Inorganic Chemistry, 4th Edition, Oxford University Press, 2006, p 77
- ²⁰ K.Kim, S.Cho, K.Yoon, J.Kim, J.Ha, D.Chun, Centrifugal vating of alumina tube for membrane application, *Journal of Membrane Science*, **199**, 2002, 69
- ²¹ Y.Chiang, D.Birnie, W.Kingery, Physical Ceramics: Principles for ceramic Science and Engineering, Wiley, 1997, Chapter 5, Single phase sintering, 403
- ²² http://en.wikipedia.org/wiki/Mohs_hardness
- ²³ <http://www.mindat.org/min-801.html>

²⁴ http://www/mcelwee.net/html/hardness_comparisons.html

²⁵ G.C.Steenkamp, H.W.J.P.Neomagus, H.M.Krieg, K.Keizer, Centrifugal casting of ceramic membrane tubes and coating with chitosan, *Journal of Membrane Science*, **199**, 2002, 69

Chapter V

Final Conclusion and Recommendations

5.1 General overview

Porous nickel membranes were produced by means of the centrifugal dispositioning technique. For the manufacture, nickel powders were successfully produced by a chemical reduction procedure, yielding nickel particles that were spherical, chemically pure which had a particle size distribution suitable for the manufacture of membranes by centrifugal dispositioning i.e. between 150nm to 1200nm.¹ It was possible to prepare a greencast by centrifugal dispositioning because the nickel particles produced during hydrothermal reduction could be formulated into a highly stable polymeric dispersion which didn't lead to membrane cracking or breakage after centrifugation. Three polymers were investigated namely polymetacrylate-NH₄, polyvinylpyrrolidone (PVP), and polyacrylamide-co-diallyldimethyl-NH₄Cl (PAAco), of which the latter was used to stabilize the nickel particles for centrifugation. The concentration of the polymer (PAAco) required to stabilize the nickel particles was 500ppm (0.5 mg/L). When this is compared to the amount of APMA used to stabilize the ceramic dispersions in α -alumina processing, the amount of PAAco used was 10 – 20 x less.² This led to a significant reduction in membrane cracking, breakage and warping. All membranes produced had a smooth uniform inner surface and could be easily removed from their formation moulds. The greencasted membranes were subjected to a sintering programme in air with temperatures ranging from 950°C to 1250°C. All membranes were sintered without any cracking, breaking or warping.

The cost of producing centrifugally dispositioned membranes decreased by about 20% when the manufacturing cost of the nickel membrane is compared to the manufacturing cost of the AKP α -alumina membranes (Sumitomo Chemical Corp, Osaka, Japan). Furthermore, nickel powders can be custom manufactured because it is made in-house. Since the manufacturing procedure is simple and fast there is no delay in obtaining the powders. The cost of formulating a dispersion of the Ni powders used in centrifugal dispositioning resulted in cost savings of up to 180%.

The characterization of the nickel membranes yielded the following results. Although the change in crystal structure and thermal expansion coefficient at sintering temperatures of 1200°C and above^{3 4}, the permeance of the membranes decreased with increase in sintering temperature. Since the porosity and average pore size remained constant initially, it could be assumed that the decrease in permeance is due to variations in the pore size distributions of the membranes and because of the formation of dead-end pores.⁵ The constant average pore size and porosity with increasing sintering temperature seems to suggest that pores were surrounded by 6 nickel particles (grains). The permeance of the nickel membrane was found to be 44 L.m⁻².h⁻¹.bar⁻¹. This compared well to

the results of Bissett who did optimization of porous α -alumina membranes manufactured by the same technique. Although the membranes showed high permeance and were able to withstand water pressures of up to 10 bar, the membranes tended to be brittle and had low tensile strength due to the intrinsic nickel oxide membranes.⁶

5.2. Conclusions

A porous asymmetrical nickel membrane was manufactured without any defects by means of the centrifugal dispositioning technique. Nickel powders were produced easily, fast and time efficiently. After a successful sintering programme, the membranes were characterized by various techniques including SEM, mercury porosimetry, XRD and water permeance. According to these results the nickel membranes had comparable properties to the α -alumina membranes with respects to water permeation. The manufacturing cost of the NiO membrane was however slightly lower than its α -alumina counterpart.

5.3. Recommendations

From this study, the following aspects require further elucidation:

- Sintering the nickel membranes in an inert atmosphere will produce nickel metal membranes which will have improved strength capabilities, and possibly improved porosity and hence permeance.
- Investigate the possibility of applying a zeolite on the inner surface of the membrane.
- Determine the catalytic properties of the membrane.
- Produce a nickel/alumina hybrid membrane and determining its catalytic properties.
- Investigate alternative nickel powder manufacturing procedures which might reduce the cost of manufacture, or improve on the properties of the membrane.

5.4. References

¹ S.S.Park, K.H.Kim, Y.B.Lee, E.Y.Choi, H.C.Park, Synthesis of nickel powders from various aqueous media through chemical reduction method, *Materials Chemistry and Physics*, **86**, 2004, 420

² H.Bissett, Manufacture and optimization of tubular ceramic membrane supports, M.Sc dissertation, North West University, Potchefstroom, 2005, South Africa, Chapter 3, Ceramic support optimization, p 33, 34

³ A.V.Bobrovskii, G.N.Kartmazov, V.A.Finkel, Crystal structure of nickel monoxide at high temperatures, *Izv. Akad. Nauk, USSR, Neorg. Mater*, **9(6)**, 1973, 1075

⁴ J.Manene, The evolution of the structure of a nickel/chromium type 80/20 alloy modified by heat, *Compt. Rend*, **240**, 1955, 2413

⁵ M.Mulder, Basic principles of membrane technology, 2nd edition, Kluwer Academic Press, 1996, Chapter 1, Introduction, p 7

⁶ http://en.wikipedia.org/wiki/Nickel%28II%29_oxide