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Investigation into the potential of membrane water treatment processes for effluent treatment and reuse within an integrated steel works

By

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Abstract

Investigation into the potential of membrane water treatment processes for effluent treatment and reuse within an integrated steel works.

This project concerns the investigation of the viability of membrane processes applied to water processing for potential recycling and reuse within an integrated steel works. Two waste streams were identified for further investigation, namely cold mill rolling emulsion and steel plant gas scrubber effluent (particulate rich), both containing variable concentrations of pollutants.

To study these processes, a versatile membrane pilot plant was designed, constructed and commissioned. This consisted of a 150 L feed tank, variable speed pump, pipe work and instrumentation with a process datalogger recording process information. Two different full size commercially available membrane modules could be accommodated, i.e. of tubular and hollow fibre formats. Three membranes were used to investigate the filtration of waste emulsion, two tubular PVDF membranes, neutral and anionic surfaces and a PAN hollow fibre. To treat the scrubber effluent, a PS hollow fibre module was used.

Experiments were conducted on two real waste streams from the works. The two real waste streams were found to have a variable composition but the membranes were able to consistently produce a high quality product stream that could have many further uses within a steel works. Water could be separated from the oil-in-water emulsion, containing several hundred PPM of oil, to produce an almost particulate free permeate containing consistently less than 10 PPM of oil, at flux rates similar to those reported in literature of 50 L m^2h^{-1} . Similarly, the filtration of the particulate bearing effluent, 7 - 122 mg / L of solids, produced water that contained less than 4 PPM of solids in the permeate at a flux rate of up to 160 L m^2h^{-1} . Due to the variability in concentration of the oil-in-water emulsion, a defined emulsion was prepared, 1.5 g / L and investigated. This gave consistently better fluxes and the key parameters investigated were variable concentration and conductivity of the solution, flow rate and transmembrane pressure. The use of 0.01 and 0.001 M K Cl having a negative effect on the permeate quality for both anionic and neutral membranes.

A cost benefit analysis has shown that a cubic meter of treated oil-in-water emulsion based effluent using PVDF tubular membranes has an operating cost of £1.17 / m^3. A cost benefit analysis has shown that a cubic meter of treated steel plant effluent using polysulphone hollow fibre membranes has an operating cost of £0.13 / m^3.

In the case of both tubular membranes, a decline in pure water flux (PWF) was seen over time, with the PAN experiencing significant permanent fouling and the PS was able to be consistently cleaned to recover PWF.

This work has shown that the use of membranes for treating waste streams of variable composition produced consistently high quality permeate and that they could be applied to treating these streams. However, further work is required to prove the full commercial viability and to assess the impact on the water system within a steel works of applying membrane water treatment processes on a large scale.

Declaration

This Work has not previously been accepted in substance for any degree and is not being concurrently submitted in candidature for any degree.

Signed (candidate)

Date 30/9/06

This thesis is the result of my own investigation, except where otherwise stated.

Other sources are acknowledged by footnotes giving explicit references. A bibliography is appended.

Signed

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I Hereby give consent for my thesis, if accepted, to be available for photocopying and for inter-library loan, and for the title and summary to be made available to outside organizations.

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1 Introduction

1.1 Work Aims

The main aim of this work is to investigate how membrane water treatment processes perform whilst filtering effluents that are traditionally difficult and therefore expensive to treat. The two main process streams identified are a waste oil-in-water emulsion and a small-particle rich effluent from steel making. A pilot plant was constructed to evaluate how membranes performed on a scale that was more representative than small bench-top experiments, whilst using actual membrane modules that are available for a full-scale filtration plant.

Investigation into the performance of the membranes as a process suitable for the treatment of the effluent was made, concentrating primarily on process operating factors. The suitability of membrane filtration to produce water of a consistent quality thus allowing its reuse/recycle was evaluated and the ability of the membrane to withstand repeated use and cleaning was assessed. The decision to filter actual effluent streams was taken due to the varying nature of a real feed and allowed the collection of operating data covering this variability. This would therefore produce information / knowledge on waste steams specific to Corus Port Talbot that could also apply to other facilities within Corus group that operate similar production plants.

1.2 Corus Port Talbot

Port Talbot is an integrated iron and steel works producing in excess of 3 million tonnes a year of rolled strip product with a current project aiming to increase capacity to 5 million tonnes. Offering a wide variety of grades and gauge, Port Talbot supplies steel to the automotive, white goods, construction and can making industries. The site, situated between

Cardiff and Swansea, South Wales, consists of a deep water harbour, coke ovens, sinter plant, blast furnaces, basic oxygen steel making (BOS) plant, continuous casting (Concast) plant, hot-strip mill, cold-rolling mill and a continuous annealing process line.

1.3 Energy Considerations

The production of steel is a very complex process requiring energy to be balanced and distributed in a careful and thoughtful manner. Gaseous by-products from the coke and iron making processes are recovered, cleaned and then burned to produce electricity and process heating around the works. Large volumes of oxygen and nitrogen, 6 million and 3.5 millions normal cubic meters respectively, are required by the works weekly and these are supplied by pipeline from a local air separation plant.

Due to the large area covered by the works and the wide spread of abstraction points around the site, pumping costs to move the large quantities of water required is significant. The further treatment of the abstracted water to standards of various qualities incurs another cost. Once this water has been used, the quality of the effluent generally requires a further processing step or steps to render the water suitable for discharge or possible reuse/recycle. Several key parameters are measured for each effluent; these typically are suspended solids, oil, pH and total dissolved solids, with analysis carried out either in-situ or via regular sampling and tests carried out by on-site laboratories. The use of membranes could have a significant effect on the water system, both amounts abstracted and quality of discharge.

Temperatures in iron and steel making can reach in excess of 2000 K so water is an essential part of process cooling. Local watercourses and the reservoir supply the raw water required for the many different users within the works. Once the water has entered the site, it is then distributed to the various treatment plants to produce water of varying qualities.

These qualities of water required vary from dock water, low saline water for once-through cooling systems, to the highest quality de-mineralised water for the production of high pressure steam, see Table 1.1.

Quality	Treatment	Main parameters	Uses
Dock water	No	Conductivity	Once-through cooling, cleaning of ships
Service water	Filtered	Suspended solids, dissolved oil, conductivity	Coke quenching, roll coolant, descale
Lime treated water (clarified)	Coagulation and sedimentation	Suspended solids, dissolved oil, conductivity	Reheat furnace skid cooling, raw feed to demin plants
Soft water	Ion exchange	Conductivity and hardness	Furnace cooling, concast and BOS cooling
Demineralised	Sedimentation, filtration and ion exchange	Conductivity	Steam production

Table 1-1Typical Water Qualities Used throughout the Works

1.4 Project Drivers

Zero discharge is a term and ideology that is used often within the wide topic of pollution control but should be re-phrased as zero-aqueous discharge when looking at industrial water usage. It can be defined as no aqueous discharge from any point on the manufacturing site. *Bryant et al [1]* covers the conceptual design of the water treatment system of the coal fired Bayswater/Liddell Power Station complex in Australia, which has a combined generating capacity of 4640 MW, to achieve zero discharge of all aqueous streams from the combined power station sites. The work focuses on the 35,600 m^3/day reverse osmosis plant and its day-to-day operation to remove the dissolved salts loading of the water systems. The paper highlights the large scale of possible membrane projects to tackle zero aqueous discharge.

Tighter water management is an area that requires a commitment from all levels of users. Targets are set each year for water companies in England and Wales to reduce leakage. In 2002/3, 3623 mega litres per day of water put into the supply in England and Wales was lost through leakage, 29 per cent lower than in the peak year 1994/5 but higher than in any of the four previous years. 'Distribution losses' includes all loses of drinkable water between the treatment works and the highway boundary. 'Supply pipe losses' is leakage from customers' pipes between the highway boundary and the customer's stop tap. Data from *Defra* [2] and is presented in Figure 1-1:

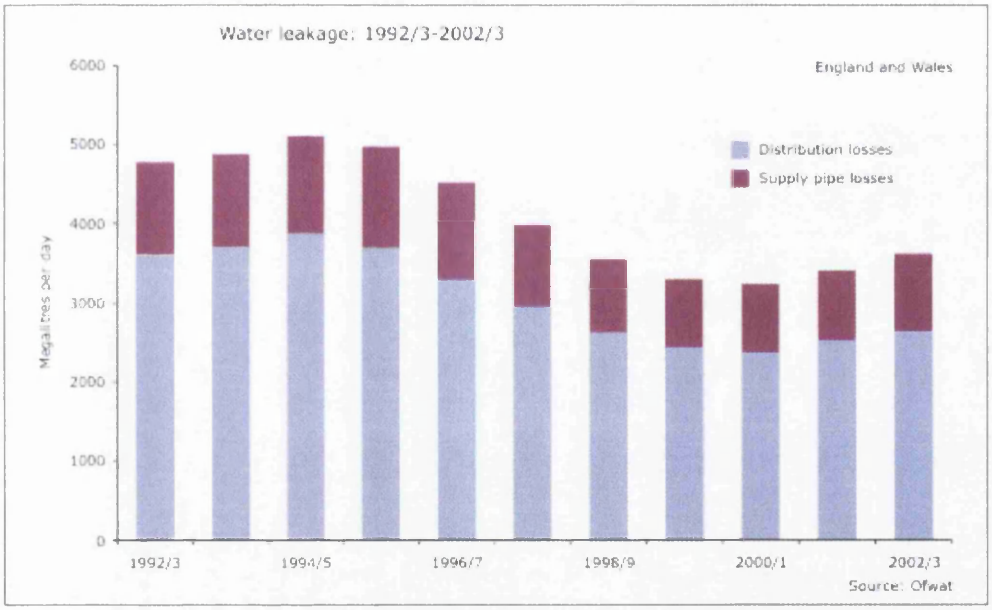


Figure 1-1 Water leakage figures by water companies in England and Wales from 1992/3 – 2002/3 - Source Ofwat

There are eight basic driving forces to reduced water usage identified by *Terrell and Holmes [3]* and are listed below:

Availability and/or Quality of Raw water

Variations in rainfall patterns have reduced the availability of good quality surface water. The last three decades have each experienced at least one major water drought that has threatened steel production in Port Talbot, notable ones occurring in 1976 and 1984. The latter causing a Water Shortage Study to be undertaken and a report produced *Gatehouse* [4]. The report contained actions to achieve reduced water consumption and the safeguarding of water supplies. This involved the identification of alternative water sources to be used when existing source quality and amounts deteriorate to levels that hinder manufacturing, re-direction of effluent to the works reservoir and several changes in treatment plant operating practices. Increasing use is being made of alternative water sources for the production of non-potable water, for example, low quality brackish groundwater is used in a study by *Smith et al* [5]. The work uses a variety of treatment methods to produce a stream that undergoes a UF/RO combination with a final re-hardening and residual disinfections to produce water for the flushing of toilets at a large entertainment complex in London. They were able to demonstrate the reduction of the domestic water requirement by 50%.

Processing and Pumping of Water

In general, before water can be used within the Works it requires varying degrees of treatment, for example via ion exchange, sedimentation, floatation and sand filtration. The water needs to be pumped from the abstraction point to the treatment plant, then on to the process, used and finally to effluent treatment, discharge or recycle. To move around these large quantities of water requires energy. By reducing the demand for water, the energy used in pumping and processing will be reduced. This can also include the careful positioning of new treatment plants to ensure that the water / effluent only travel the least distance for treatment.

Cost of Raw Water

Increasing demands for higher quality drinking water and cleaner in-shore waters, have led to very large capital investments by the water supply companies and this cost has subsequently been passed on to the consumer, both industrial and municipal. The capital investment plan for Welsh Water, covering 2000 to 2005, is in excess of £1200m, *Welsh Water [6]*. The cost of water abstraction is expected to rise but at current levels supplied to the works, with the average cost of abstracted water at 0.47p/m^3 for Port Talbot Works, there are currently no major economic benefits that can justify large scale.

The introduction of Integrated Pollution Prevention Control (IPPC) [7] *IPPC Directive (96/61/EC)*, will pose new operational challenges, with the general aim being to reduce waste at source taking into account noise and pollution to air, water and land. IPPC will bring about changes in pollution control, with a potential impact on operations. Unlike previous legislation (Integrated Pollution Control), waste reduction and energy efficiency will be included, Environment Agency [8].

Ability to discharge

Where surface and ground water have to be used for potable water, the discharge of industrial effluent into a watercourse near abstraction points may be prohibited. This is a possible restriction to inland sites but with the coastal location of Port Talbot, discharge to the sea is used with no downstream municipal or industrial users of the water. Due to the particular tidal nature of the Bristol Channel, with a high tide in excess of 14m in parts, companies discharging into it argue that it is able to distribute any pollutants entering into it and thus preventing any localised build up. The turbulent kinetic energy generated by the tidal current is sufficient to keep the Bristol Channel proper vertically well-mixed throughout the year *Pingree and Griffiths [9]*.

Discharge consent limits

Discharges are very stringently controlled and monitored by both the Environment Agency and the Environment Department of Corus. Over the last 20 years the tightening of the consents has led to large investments by companies in building treatment works to meet the existing consents and any likely further restrictions. As more sensitive analytical equipment has been developed which can detect elements down to parts per billion, the consents have been revised downwards and proven polluting chemicals have been identified and subsequently their removal has been required. This has led to the addition of new process equipment into the existing treatment plan and with it, further associated capital and operating costs. Again the coastal location of the works has been a benefit in the setting of discharge consents, this has recently gone from a volume to a mass based consent using mass of monitored determinant/month as units. From the 1st of January 2005, significant reductions in several determinants have been agreed some of which are:

- 17 % in the total allowed suspended solids discharge in a day
- 29 % in the total allowed oil discharges in a day
- 40 % in the total allowed ammonia discharge in a day
- 38 % in the total allowed Phenol discharge in a day

"End of Pipe" versus Point Source Treatment

Investment in new effluent treatment plant is generally viewed as non-productive but essential by most industrial sectors. The main cost of treatment plant is mainly based upon capacity and they are normally over sized to allow for plant upsets and some flexibility in incoming flow rates. The increasing costs of effluent treatment provide an added incentive for the reduction and or re-use of water so that the size of the plant constructed is optimised. This approach of water reduction and re-use needs to be considered when designing new treatment facilities and can lead to huge economic savings and in certain circumstances, remove the need for the new plant altogether.

The traditional end-of-pipe treatment works is a large and mature facility that offers a unilateral decoupling between the production and treatment systems, *Zotter [10]*. Moves are being made to look at point source treatment that offers a more specialist and focused treatment for the primary pollutant of that source. The idea is to treat an effluent when it's contaminants are still concentrated and in a relatively pure form i.e. before it is diluted and mixed many times with various other effluent streams. This should allow more reliable plant to be designed as the number of possible pollutants is reduced and can be predicted with more certainty and the flow rate to the specific plant is lower so the equipment required is smaller and therefore cheaper. For example, if a pressure driven filtration process was employed, the pumping costs are directly related to the volume being filtered.

Rising Environmental Costs

The introduction of the EC Directive on IPPC will directly impact on the control of polluting activities. The control of currently unregulated processes will be phased in by around 2007 in placing an increasing emphasis on the 'polluter pays' principle. In 1998, ICI at Runcorn, was fined £300 000 for a groundwater pollution incident which to date is the highest fine imposed by the North-West Environment Agency. In a report by the *Environment Agency [11]*, it stated that fines had increased by 36% and the number of prosecutions up by 18%. In the North West Region during 2003, a total of £710,065 in fines and £237,768 in costs were imposed on environmental offenders.

Company Image

The importance of some companies to have a publicly conceived green image is having a positive effect on the acquisition of funding for projects which will actively improve the local; and to some industries, the world environment. Public pressure from the towns located around Port Talbot and Llanwern has led to significant reductions in air pollution even when discharges have been within the levels set by the Environment Agency. All complaints from neighbouring residents are logged internally with the Environmental Department and then reported to the Environment Agency detailing reasons / causes for the incident.

Some companies are prepared to use the environment as part of their marketing strategy. Instead of just protecting their image by meeting all consent requirements, these companies believe that there is a competitive advantage to be had by exceeding the benchmarks set by their competitors. This has seen the introduction of Environmental Management Systems (ISO 14001) that are independently audited by an external source and are systems that allow the environment to be managed in the most efficient way practically possible. This factor is industry dependent but now some companies, for example, Land Rover (UK), is expecting all its tier one contractors to gain ISO 14001 certification. Work in this area has been gathering momentum within Port Talbot; recently the Coke Ovens and the Energy Department have been accredited with this standard.

1.5 Summary:

- Even though water is cheap, its supply is not limitless.
- Due to the vast quantities of water used, the energy required to move water around the works is large.
- Although fairly well placed for the disposal of water, the consents for discharge are becoming more stringent.

2 Background to Water Usage in Port Talbot Works

2.1 Raw Water Supply

The majority of the following flow rate data was obtained from a report prepared by British Steel Consultants in December of 1995 at the then current production levels of around 3 million tonnes, *British Steel Consultants* [12]. The amounts of water quoted are not absolute and serve only as an idea to the quantities and qualities of water used within the works.

The main sources of raw water to Port Talbot Works come from rivers, namely the River Afan, the Ffrwd Wyllt and the River Kenfig, plus the Castle Stream (Tydu) that feeds the Eglwys Nunydd (EN) Reservoir, see Figure 2.1. Several streams drain from the moor areas to the east and south of the works into a system of ditches and culverts.

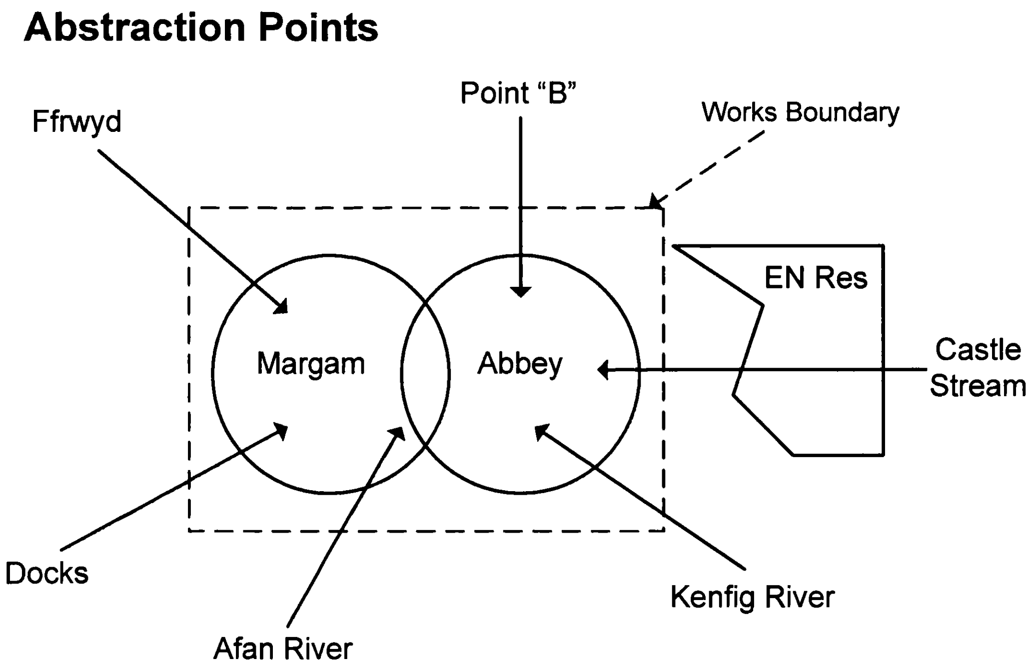


Figure 2-1 Local Water Courses and Reservoir Overview

River Afan

The River Afan flows down Cwm Afan from the Rhigos Mountain to the area of Port Talbot's docks. There is a weir upstream of the river mouth and the Afan water is abstracted from a position upstream of this weir, through a feeder canal to the works pump house and the canal overflow then flows into the dock. The pump house inlet position, upstream of the weir, results in minimum salt-water contamination of the abstracted Afan water, except in times of very exceptional high flood tides backed by westerly winds.

The Afan water is pumped throughout the works, with major off take points at Margam "C" Demineralisation (Demin) Plant, the Abbey Soft Water Treatment Plant, the Continuous Caster (Concast) open spray systems, the cold mill pickle rinse (via treatment plant), and the main pump house (MPH). The pH, chloride content and the conductivity values monitor quality of this water to the works.

Ffrwd Wyllt

This water source is abstracted at a pump house at Taibach and is pumped to a system linked closely to the River Afan distribution system. Currently the Ffrwd Wyllt is used to top up the blast furnace cooling systems and has emergency supplies to the demineralising and soft water treatment plants. Generally clean and of good quality, the Ffrwd Wyllt abstraction point does not suffer from any ingress of salt water. The river flows into the docks, from which water is abstracted for process and plant use.

River Kenfig

The River Kenfig flows south to Kenfig Hill before turning west to the north of Pyle, through an area of sand dunes to the sea. The River Kenfig abstraction can either be pumped directly to the EN Reservoir or to the Point "B" sump. The River Kenfig supplies a number of other industrial users (Kenfig Industrial Estate) and abstraction is controlled by the Environment Agency. Castle (Tydu) Stream is a feeder to the River Kenfig but is also used as a feeder to the Eglwys Nunydd Reservoir. The water is fed from a weir like sump with a fixed open pipe from the sump flowing to the reservoir. This stream has large seasonal variations in its flow and chemical analysis; the winter months see high quality water with high flow and adequate abstraction to the reservoir. However, in periods of drought, the flow is reduced and quality deteriorates usually in the form of higher conductivities and in the pick-up of chloride ions.

Eglwys Nunydd (EN) Reservoir

The EN Reservoir is fed from a control weir in the Castle stream, when full, the water level is ~12 m above sea level, under emergency conditions, i.e. in years 1976, 1984 and 1995 it has been lowered to its limit of 6.25m above sea level. A manually controlled discharge from a low level sluice gate feeds water by gravity to Point "A" of the works drainage system. When the reservoir is full, the discharge is controlled to maintain a water level some inches below the overflow weir; this provides a safety margin for storm conditions when the reservoir would collect water to add to that in the works drainage system.

Upper and Middle Mother Ditches

-Upper Mother Ditch

Water from the agricultural and moor land areas to the east of the works drains into the Upper Mother Ditch. As with the other natural water supplies, the quantity and quality of the water is affected by the climatic conditions as well as the use of agricultural chemicals and practices.

-Middle Mother Ditch

Water south of the works drains into the Middle Mother Ditch. This includes natural drainage from moorland / marshland area and drainage from the coke oven coal stockyard area which can affect water quality.

Docks

Associated British Ports (ABP) have sealed the old Port Talbot Dock by replacing the dock gates with sheet piling forming a fresh water reservoir. The dock receives water from the Ffrwd Wyllt and the overflow from the pumping station on the Afan River feeder and the level is maintained by introducing seawater when feed water is low. The main use of the water is for blast furnace slag quenching and a re-circulating cooling system for the three turbo-alternator condensers. At low water levels, there is an increase in salinity (i.e. when the Ffrwd Wyllt is low) as the water is abstracted from the River Afan mouth to the docks and this tends to be brackish.

Other Sources

Due to the size of the Corus site, there are a number of small streams, springs and drainage areas that run into the works boundaries. Often in periods of high rainfall these constitute a flood situation and have to be pumped from the various satellite sumps out to sea via No.2 Effluent sump. There is also the River Arnallt which flows into the middle of the works, Corus do not have an abstraction licence for the River Arnallt and have diverted the flow direct to sea via the Arnallt sump. In times of flood or high river levels, the Arnallt flow can increase dramatically and contains considerable debris. The Arnallt also tends to accumulate various effluents as it flows through built up urban areas and parts of the Works site. Recently efforts have been made to improve the quality of the Arnallt and it could possibly assist Corus in times of shortage, however the flow would be very low under these circumstances.

Water Quality and Monitoring

Water quality of the raw water feed is not measured and recorded automatically, instead daily, weekly or monthly measurements and pro-rata calculations for a given period using basic techniques are made. There is little metering of any of the internal plant water flows, with no real measurement of usage in any of the works areas. There is some flow measurement of process waters, e.g. Concast plant / Basic Oxygen Steel making (BOS) plant cooling water flows but there is no method of regularly recording flow and consumption details.

Feed sources and effluents are measured at approximately 90 points by technical departments and contractors and are routinely reported to the energy, environmental or the works production units. Very few of these measurements are made on-line and therefore, real time or accumulated data is not readily available. Recently efforts have been made by work's areas to improve the amount of flow metering on site to facilitate accurate mass and energy balances.

2.2 Water Treatment

The water entering the works is directed to certain treatment plants that produce the particular quality required for specific parts of the works. The flow rates quoted in the following sections are from the *BSCOS Report*, with the majority of the flows being estimated from pump capacity and run time or via the use of portable flow meters.

Demineralisation

Within the Works, four plants are used to remove molecular ions from raw water sources with the required quality dependent upon the end user. Two basic types of demineralised water are produced: softened and demineralised water, the latter can also be further treated to produce polished water used for power generation.

Abbey Soft Water Treatment Plant

The treatment plant receives River Afan water as its normal source with works service water as an emergency supply. The plant can supply soft water at rates up to 160 m^3/hr. The raw water is passed through two stages of settling to remove suspended solids. In the second stage of clarification, flocculent is added in the clarifier with the clarified overflow passing to four sand filters. The filtered water passes to three cation exchange vessels (via two storage tanks) where the dissolved salts are chemically transformed into sodium salts, i.e. soft water. This is achieved using a sodium-based resin that exchanges the calcium and magnesium ions for sodium ions. The main users of soft water are the hot mill reheat furnaces, the BOS plant hood and lance cooling system and the caster units.

Abbey and Margam Demineralisation Plants

The Abbey Demin Plant is next to the Abbey soft water treatment plant but currently receives its water from the cold mill lime treated water plant (some 2 km away). The plant is capable of producing about 200 m^3/hr water using the cleared (filtered) cold mill water. The water passes directly into a raw water tank that feeds into the cationic and the anionic exchange units. The water, having a high pH at this stage, is then sent to one of two storage tanks that then feed the five pumps that distribute the water to consumers. The main users are the cold mill for preparation of rolling emulsions, the service boiler house for steam generation and the Margam C Demin Plant.

A network of pipes connects the three Demin Plants so that water can be transferred between them in the event of an emergency. The other users are the Concast plant for mould and roll cooling systems and in the blast furnace area. For the Margam Demin Plant, raw water is supplied from the River Afan and demineralised water is supplied to the boiler plant. The Margam Demin Plant is currently operated for one shift (12hours) per week only.

Margam "C" Demineralisation Plant

Demineralised water can be produced at rates up to 200 m^3/hr when required. The feed water is supplied from the River Afan and in emergencies from the Ffrwd Wyllt. A primary settlement tank is used to remove large settable solids and allow flow equalisation. Next, the water is fed into a clarifier and dosed with polymer, this clarified water then passes to a sand filter station where finer particulate are removed. Three stages of cationic/anionic/mixed exchange are used producing water of very low conductivity that is stored in an intermediate stock tank before passing to two further stages of final polishing. At the intermediate stage, water from Margam and Abbey Demin Plants can be introduced. The water is mainly used to supply the Margam and Mitchell boilers and is used for the production of electricity.

Cold Mill lime water Treatment Plant

The raw water supply to the treatment plant is from the River Afan and during emergencies (i.e. when the River Afan has a very high conductivity or there is a supply failure) water can be taken from Point "A" or from the works service water system. The maximum output of the plant is about 300 m^3 / hr. The water is clarified using flocculent for settling the large solids and then filtration to polish it. The main user of the treated water is the Abbey Demin Plant, which uses it as a raw water supply. The smaller users are the slab reheat furnaces (cooling system), the hot mill motor room (cooling system) and as make up to the pickle line rinse system.

General Service Water

This low quality water is used for general duties, e.g. fire fighting and cleaning, and for descaling of strip metal in the hot mill. As this process uses large quantities of water, the system consist of a recycle loop with an initial clarification plant and then a series of settling canals to further reduce solid contamination and skimming of free oil. The clarified water from the canals is then sent to a set of sand filters and recycled.

2.3 Water Users

Iron making

Water in this area is used mainly for cooling and gas cleaning. During coke production large quantities of service water are used for coke quenching. Since the installation of Number 4 effluent sump, this has been supplemented by treated effluent from the sump. The sinter plant and harbour areas use small amounts of service water for cleaning etc. Slag quenching, gas cleaning and cooling in the blast furnace areas use a mixture of river and dock water. Estimates for the cooling requirements have been placed at around 330 m^3 / hr with all effluent going to No.2 sump. Gas cleaning uses dock water with estimates of 480 m^3 / hr for both furnaces. Slag quenching requires approximately 900 m^3 / hr with 70% being sent to a drainage sump and onwards to No.2 sump.

Steel making

The steel plant uses on average 300 m^3/ hr of service quality water taken directly from the works reservoir for gas cleaning, 5% of which is estimated to be lost through dust sent to the tip and evaporation. The effluent contains solids carry over which prevents its immediate reuse in other processes so is sent to either No.4 sump or No.2 sump. The hood and lance cooling in the steel making process is maintained using soft water with losses incurred during cooling tower operation and blow down. Approximately one third of all soft water production is used here. Soft water is also used for cooling of lances and flanges, ~12 m^3/hr, in a closed circuit cooling tower system. During casting of the steel slab a mixture of demineralised and soft water is used to cool the mould, with an open spray cooling system using clarified Afan water to cool the slab surface.

Hotmill Area

The hot mill area is the largest consumer of works service water, approximately 972 m^3/hr is lost from the system (equal to ~ 45% of all service water use). The flows are very high, up to 4500 m^3/hr to the primary filters and almost double that amount returned to the sedimentation tanks in the form of "dirty water return". Filtered water (via sand filtration) is used for roll coolant, scale breaking, down coiler cooling cross sprays and inter stand cooling. Much of the water is recycled through sedimentation tanks, clarifiers and sand filters, all of which is required to maximise water recovery and product quality, by ensuring system breakdowns are kept to a minimum through reduced nozzle blockages etc.

The skids are cooled using a combination of Abbey soft water (40 m^3/hr) and cold mill treated water (35 m^3/hr). Soft water is also used on the Run Out Table to control grain size and crystallisation during the rolling of Hot rolled products, see Figure 2.2. The other cooling requirements are carried out using service water (35 m^3/hr) with excess water from the system going to the flume and onto the scale pit. Other losses are from the cooling towers.

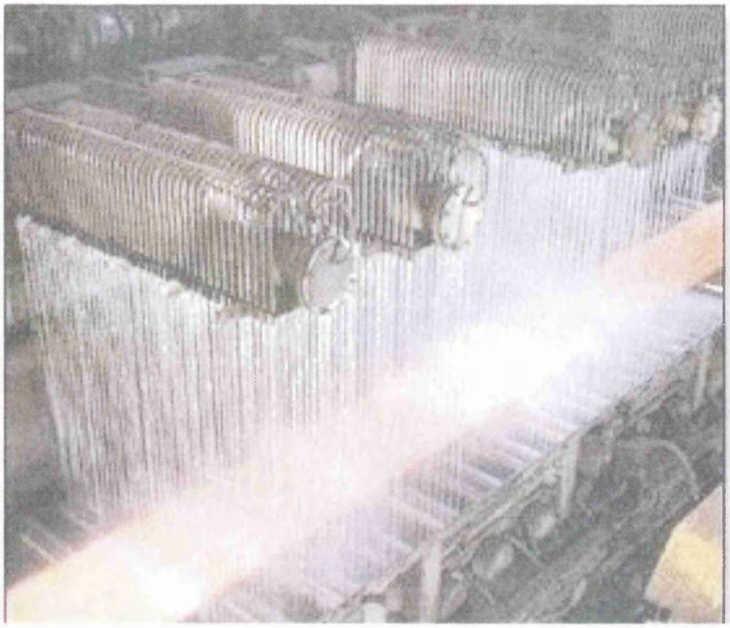


Figure 2-2 Run out table – Port Talbot Hotmill

Cold Mill and Continuous Annealing Plant (CAPL) Area

Approximately 410 m^3/hr of service water is used throughout the area for several duties, including cooling in heat exchanger networks, cooling towers and coil quenching. A mixture of cold mill lime treated water and service water is used to rinse the coil surface after the pickle line, this produces a highly acidic iron bearing waste. Cooling of the rolls is undertaken using demineralised water and this is also used to produce oil-in-water emulsion that acts as a lubricant.

The effluent produced is very variable with oil concentration being an important parameter. This effluent would be applicable to membrane water treatment processes as the treatment of oil-in-water emulsions is an area of where membranes have been used successfully to produce a consistent effluent quality, this is discussed in more detail in chapter three. The CAPL system has its own water treatment plant to supply demineralised water and process any effluents produced in the process. A small stream of treated water is sent to No.2 sump.

2.4 Effluent Systems

There are eight effluent sumps in Port Talbot with another two sumps that are used to collect water from all the other sumps, namely No.4 and No.2 sumps. Table 2.1 details some key parameters of the first eight sumps with samples taken over a four-month period by the Energy Department. The effluent produced by the rolling mills is not listed within this table. Due to its specialist nature, the effluent does not enter into the general effluent system until it has been fully treated. Figure 2.3 gives the broader layout of the effluent system and how they interconnect.

Effluent Source	pH	Suspended Solids / ppm	Conductivity / μS/cm^2	Oil / ppm
No.1 Margam	8.5	95	750	20
No.5 BOS	8.0	60	400	10
BOS Storm Water	10.5	35	800	12
Clarification Plant	7.8	80	350	20
Deep Drain	9.0	65	1,200	
No.10 Morfa	8.2	45	720	23
No.6 Grange	8.0	53	750	25
No.3 Sump	7.5	30	350	10

Table 2-1 Four Month Average analysis of individual effluent sumps.

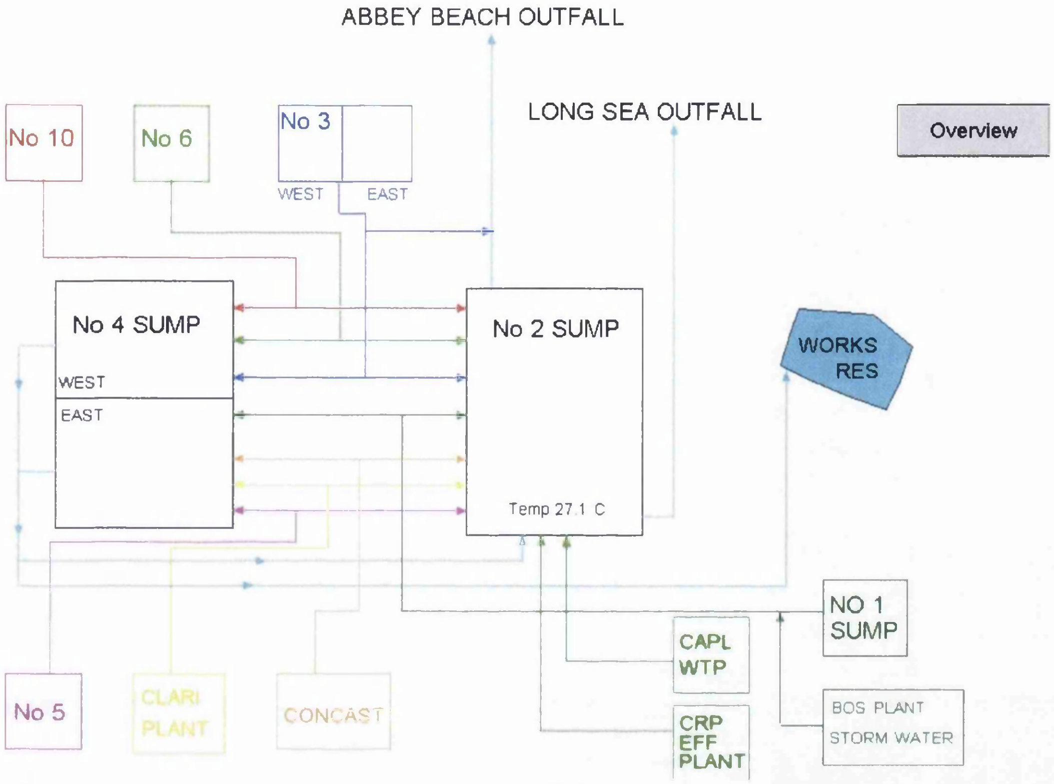


Figure 2-3 Port Talbot Steelworks Effluent Sump system.

No.4 and No.2 sump

Two sumps that are not mentioned in Table 2.1 are No.2 and No.4 Sumps. The original design concept of No.4 Effluent Sump was to remove solids from the effluent streams prior to discharge to sea via the use of polymers to settle out any solids in the streams with the residence time and flow design to allow solids to flocculate and settle out within the sump.

The sump is periodically de-sludged and the sludge allowed to dry, during down time of the works, the sump is also dug out to remove the more compacted sludge from the bottom. Only after construction was the idea of effluent treatment and recovery from the sump realised. Work has been done to look at different uses that the effluent produced from this sump could be put to. Coke quenching and dust suppression were some of the earlier uses due to the requirement for low quality water. As the quality of water produced from this sump was found to be consistently good, the effluent was being redirected to the internal works reservoir. No. 2 sump is used as a buffer for flow management whilst discharging to sea.

No. 3 Sump

No3.Sump effluent, fed mainly by surface and storm drainage, is an obvious choice for recovery but the flow varies depending on weather conditions. A number of sumps have emergency overflows that flow into No.3 Sump and overflow of these sumps is possible during periods of heavy rain. The excess rainwater will dilute the contaminant loading of the effluent, except for suspended solids. This is because heavy rain will cause run-off of coal dust associated with drains that link into the Coke Ovens effluent sumps from coal stock yards. This could lead to problems with effluent recovery.

No.5 BOS Effluent

No5 BOS Effluent is mainly blow-down from gas wash water produced during the steel making process and local surface drainage. During heavy rain periods, washings from the local drains keep the solids at a relatively constant level. Heavy contamination of this system occurs during steel plant maintenance periods, especially where the gas wash water treatment plant is completely blown down and de-sludged. This occurs for no more than two one-week periods a year. To mitigate the effect of this, recovery of water from this effluent source can be avoided during these periods. The average concentration of suspended solids is relatively low at 60 PPM but does vary widely in use.

Clarification Plant

Clarification Plant effluent is cooling tower water blow down and filter backwash water from the Continuous Casting Plant (ConCast). The raw water source for the ConCast is either treated softened water or River Afan water. Afan water is the best quality raw water source available to the Works. During use, this water picks up suspended solids and oil. Due to it's pH and conductivity, an ideal effluent for recovery treatment and reuse although does contain relatively high oil concentrations, 20 PPM when compared to the No.5 BOS Sump.

2.5 Stream Selection

Within Port Talbot steelworks there exists opportunities to use every different type of membrane process. To address the needs of water recovery, the treatment processes selected for further investigation had to be capable of handling large flow rates under economical operating conditions. Streams were therefore chosen that required either minimal processing to produce a quality of water that was immediately re-usable or was the cause of a specific pollutant problem.

The No. 5 BOS effluent was chosen as it contained relatively low conductivity and minimal oil concentration. The cold mill effluent plant was recognised as an area where the existing process stream was difficult to treat and control with the resulting treated effluent being a major source of oil contamination at times due to the unreliable treatment process employed. Ultrafiltration / microfiltration treatment processes were highlighted as processes that were able to produce consistently high quality permeate streams from these two types of streams, despite the possible variations in contaminant loading of the feed.

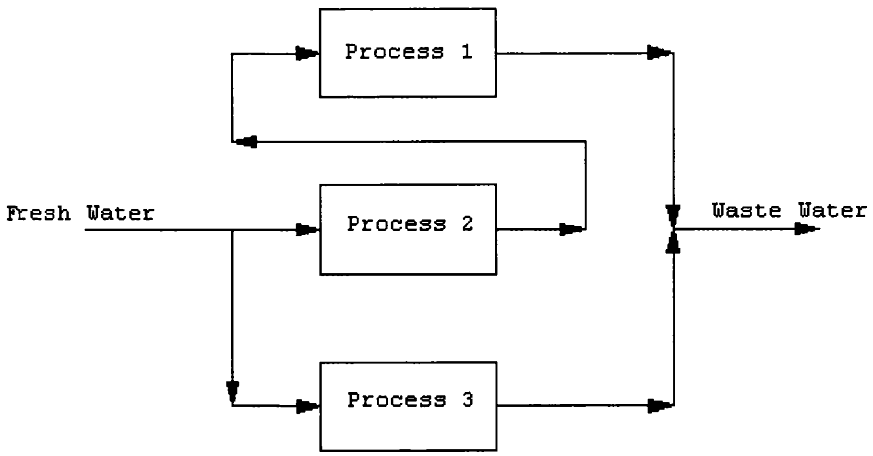
3 Literature and Technology Overview

The following chapter presents some general techniques that can be used to recover / reuse water and problems relating to their use within the steel works. A background to membrane technology is also given, concentrating initially on the technology in a broad and practical sense, and then using specific sections to give a more thorough review of the use and limitations of membranes on the process streams to be investigated.

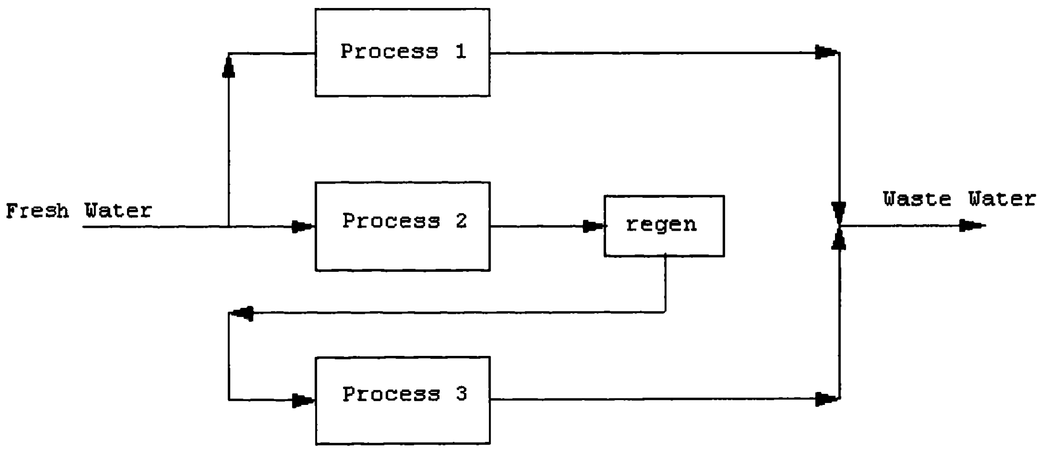
A thorough literature review of applicable models to the membrane filtration process is given by *Bowen and Jenner[13]* and gives guidance on which models are applicable to certain streams.

3.1 Approaches to Water Minimisation

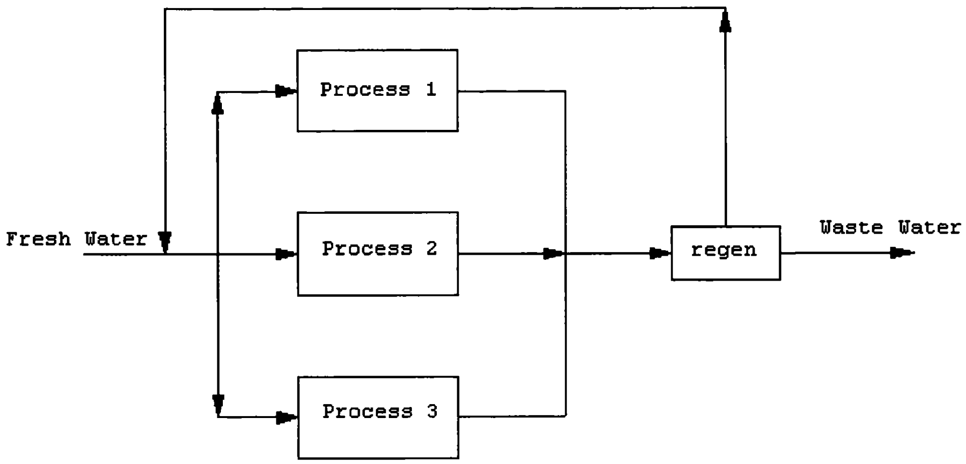
There are four basic approaches to water minimisation, taken from *Smith [14]*, three are presented in Figure 3.1 with the fourth approach via actual process modification. Process changes are the introduction of a different process to perform the same task as the original process but with an inherently reduced demand for water. Examples of these in the steel industry are the use of electrostatic precipitators instead of wet scrubbing towers for the removal of air borne particulates, or the use of forced draft cooling towers instead of natural draft. Changes to the actual manufacturing route can also be introduced so that water is used more efficiently, optimisation of cooling sprays on the run out table via more accurate heat transfer coefficients would allow much tighter control over the amount of water used.



(a) Reuse



(b) Regeneration - Reuse



(c) Regeneration - Recycle

Figure 3-. Approaches to water minimisation

In Figure 3.1 (a), water is initially used in Process 2 that has a demand for high quality water. It is then re-used in a process, Process 1, which does not require water of the same quality initially supplied. This "wastewater" from Process 2 can only be used if the contaminant loading does not affect the second process in anyway. This approach does not substantially reduce the pollution loading but will reduce wastewater volume and freshwater consumption.

Via the introduction of a partial treatment stage so that the water is of sufficient quality to be re-used in another process, water can be re-used as in Figure 3.1(b). The regeneration stage is any operation that removes the contaminants that prevent the water from being re-used, these can be filtration, precipitation / separation and so forth. Regeneration re-use reduces freshwater and wastewater volume and the pollution load is reduced via the introduction of regeneration (that is the aqueous pollution load as generally a solid waste is produced). It should be noted that the water does not re-enter the same process where it was originally used.

Another approach is to use a regeneration stage to remove contaminants and the water produced is then of a quality that can be recycled in several different processes, including ones that were originally using the water, one such arrangement is shown in Figure 3.1(c). Freshwater and wastewater volumes are reduced and wastewater load is reduced via the regeneration stage. This is different to regeneration re-use as recycling can lead to the build up of specific contaminants which may reach concentrations undesirable for any process and require a direct purge to remove them or alternative treatment scheme to allow the continuation of water re-use.

3.2 *Numerical Approach to Water Reuse – Pinch Procedure*

A technique exists that allows the optimisation of water-use to be achieved by using a systematic design procedure. This procedure is generally referred to as Pinch Analysis, *Doyle and Smith [15]* and *Wang and Smith [16]*. This technique was originally developed in the 1970's for the optimisation of heat exchanger networks and it is the analogy between heat and mass exchange that allows the technique to be extended to water systems and its distribution.

The prime objective of Pinch Technology is to achieve financial savings by optimising the ways in which process utilities (particularly energy and water) are applied for a wide variety of purposes. Pinch Technology does this by making an inventory of all producers and consumers of these utilities and then systematically designing an optimal scheme of utility exchange between these producers and consumers. With the application of Pinch Technology, savings can be achieved in both capital investment and operating cost, whilst emissions can be minimised and throughput maximised.

For this technique to be applied, an extensive knowledge of the water requirements in terms of water demand and the upper limits of the defining quality parameters of each process is needed. This knowledge can then be applied so that water streams can be directed to a particular process that can use the water without treatment. After its initial use, there may exist another process that is able to use the effluent created due to the process not demanding water of a quality higher than the effluent leaving the original process.

The pinch technique is now becoming a mature and recognised approach for water reuse that can identify and generate possible solutions for a more efficient water distribution network in terms of amount of water used overall. This technique was applied to a process plant owned by Monsanto in Newport, Uk, where savings of $1Million were identified by Linnhoff-March Consultants including in-process modifications. These changes significantly reduced the size of the new effluent treatment facility as well as giving an immediate benefit in operating cost savings, *Environmental Expert* [17].

The drawback of this technique when applied to the Port Talbot works is that the geography is such that pumping costs between suitable processes may override any benefits of water reuse on a site wide nature. An initial, phase Zero Study of Port Talbot Steelworks by *Linnhoff-March [18]* concluded that the technique was not deemed feasible at current water costs due to the disparate layout of the treatment and effluent systems.

3.3 Membrane Filtration Water Treatment Processes

General Description

A traditional definition of membrane filtration is:

"The separation of the components of a pressurised fluid performed by polymeric membranes." *Paulson and Jondahl [19]*.

With the widespread development of non-organic materials, this definition is slightly dated but still applies to the majority of membrane processes. The openings in the membrane matrices (pores) are so small that significant fluid pressure is required to drive liquid through them and can be split up into four different areas, reverse osmosis, nanofiltration, ultrafiltration and microfiltration.

Process	Operating Pressure	Separation Size Range	Uses
Microfiltration	< 3 Bar	10 – 0.1 µm	Slurry thickening
Ultrafiltration	< 6 Bar	< 0.1 µm – 5nm	Emulsion treatment
Nanofiltration	< 9 Bar	Bi- & tri-valent ions	Water softening
Reverse Osmosis	8 – 60 Bar	Monovalent ions	Demineralization of water

Table 3-1 Classification of Membrane Separation Processes for Liquid Systems

Crossflow filtration is used to describe the basic set-up of the majority of membrane processes. The pressurised feed flows across the membrane surface with a portion of the feed permeating the membrane whilst the balance of the feed sweeps parallel to the surface of the membrane to exit the system without being filtered. The filtered stream is the "permeate" because it has permeated the membrane. The second stream is the "concentrate" because it carries off the concentrated contaminants rejected by the membrane, see Figure 3.2:

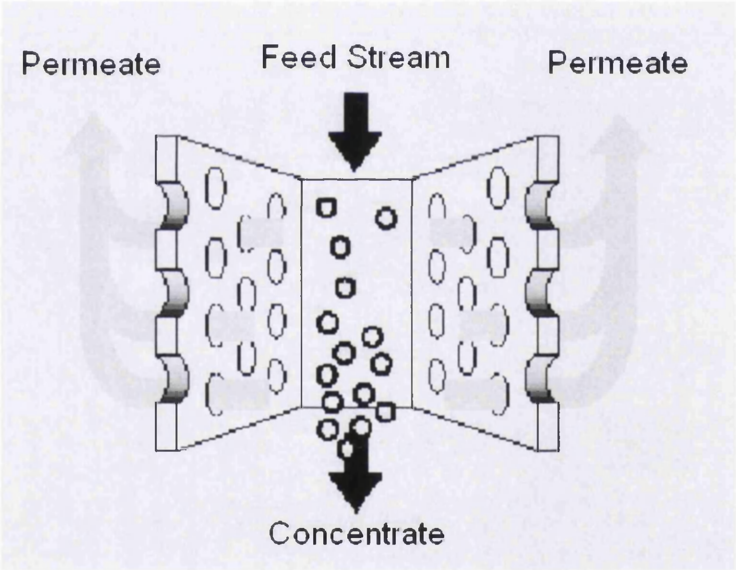


Figure 3-2 Principles of Crossflow Membrane Filtration

The crossflow operation allows the continuous removal of cake or surface contaminants that in "normal flow" filtration would cover up or plug the membrane pores very rapidly. Therefore, the crossflow mode of operation is essential for the most efficient use of the membrane.

The majority of membranes are of an asymmetrical structure, see Figure 3.3, so that the inside layer of the membrane that actually filters the process stream can be kept as thin as possible. This layer is then supported by a thicker and more porous layer of the same material that allows permeate to flow as easily as possible to the outer shell of the membrane and away whilst giving the membrane more mechanical strength. By using this design, the total resistance of the membrane is also minimised as the higher resistance inner layer thickness is reduced.

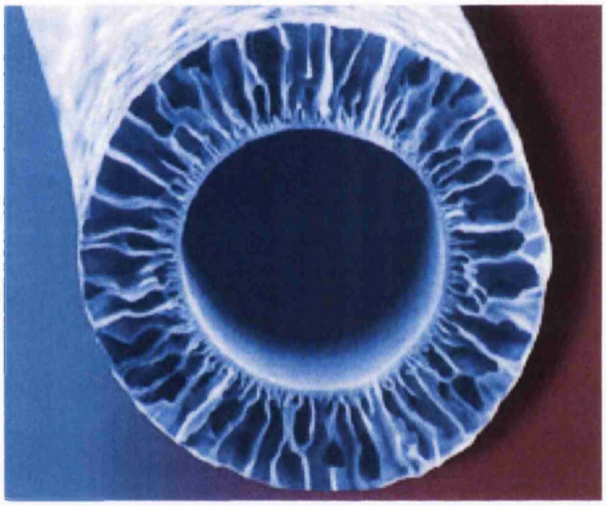


Figure 3-3 Scanning Electron Micrograph of an Asymmetrical Membrane Structure Koch Membrane Systems [21]

Thin-film composite membranes also exist where an ultra-thin film is deposited on a porous support and is cast upon a supporting fabric; see Figure 3-4, *Joshi et al [22]*.

Figure 3-4 Schematic Diagram of a thin-film composite membrane *Joshi et al [22].*

Membrane technology is generally perceived as a specialist technique for the filtration of specialist wastes / products but in reality they are becoming a mature alternative, *Bilstad [23],* with many extra benefits due to their compact size and ease of operation, *Cheryan and Rajgoplan [24].* In the year 2000, the total European market for membrane separation systems in industrial process water treatment, was US$198 million (~44% of the total industrial market) with expected growth to take this up to US$382 million by the year 2007, *Frost and Sullivan [25].* A more recent report from *Chemical and Engineering News 2003 [26]* estimates that the total demand in the U.S. for membrane systems, including associated pumps, pipes, and vessels, is projected to approach US$6 billion in 2006. This demonstrates the acceptance of membrane separations as a valid alternative to traditional methods; highlighting many further opportunities and needs for research in membrane technology.

Reverse Osmosis

Pores in this membrane class are so small they have not been resolved either by scanning electron or atomic force microscopy. The pore diameter is theorised to be somewhat smaller than twice the thickness of the pure water layer that occurs over the membrane, *Sorirajen [27].* This pure water layer is void of ions and through this exclusion "rejects" the ions, preventing them from permeating the membrane.

Many large-scale RO plants are in existence, with the largest example in Britain operating on the island of Jersey, *Marsh et al [28].* The plant is designed to desalinate seawater to produce a daily output of 6000 m^3/day from a feed water quality of ~38 000 mg/l TDS. A recent contract awarded by the Israeli Government, *Filtration and Separation [29]*, is valued at US$800 million to build, operate and transfer a membrane seawater desalination plant. The plant is to supply 50 million cubic metres of drinking water per year and is being described as the world's largest reverse osmosis desalination facility. Large-scale plants are not new with a plant capable of producing 70 000 m^3/day being designed for a Middle Eastern city in 1977, *Finlay and Ferguson [30]*.

The process used to treat lower TDS waters is called Ultra-low pressure RO, ULPRO, with operating pressures around 7-10 bar and have established themselves as state-of-the-art products with excellent performance, reliability and predictability, *Filteau and Moss [31]*. An obvious advantage of ULPRO is their lower operating pressure and subsequent lower operating costs than high pressure "traditional" RO plants.

Nanofiltration

Nanofiltration (NF) equipment removes organic compounds in the 250 to 1000 molecular weight ranges, also rejecting some salts (typically divalent) and passing more water at significantly lower driving pressures than RO. NF economically softens water and reduces the pollution of regeneration systems. They also provide unique fractionation capabilities such as organics desalting to preferentially remove semi-volatile organics against volatile organics from mixed solutions, *Agenson et al [32]*. They essentially operate under the same principle of RO but the membranes allow the passage of salts and organics.

To date the largest application of NF membranes is for removing hardness and dissolved organics from water, *Raman [33]*. This ability is widely used in drinking water production, examples of which are in the NF of eutrophied lake water in Taiwan, *Yeh et al [34]*, ground water remediation in Japan, *Ratanatansku et al [35]*, and the removal of colour from surface water in Scotland, *Irvine et al [36]*. In each case, NF was preferred to traditional water treatment schemes due to consistently high permeate quality within stringent limits set for water required for human consumption; even with a variable quality in feed water. When operated at pressures of 0.5 – 0.7 MPa, *Watson et al [37]* reported rejection of 85 – 95% of the hardness and over 70% of the mono-valent ions when treating a coloured drinking water source in Florida, USA.

NF is also being used in combination with RO to increase the recovery of wastewater that would be un-economical with just RO, especially in areas where a "zero aqueous discharge" policy is employed, *Rautenbach and Linn [38]*. The ability of NF to seemingly preferentially allow the passage of mono-valent ions when in mixtures with multivalent ions has brought about research for its use to filter landfill leachates, *Linde and Jonsson [39]*. The retention of heavy metals was found to be high whilst maintaining high fluxes due to the passage of mono-valent ions resulting in a lower transmembrane osmotic pressure. This also makes it useful for the recovery and regeneration of cleaning chemicals like NaOH, allowing the cleaning-in-place solution to maintain constant cleaning efficiency, minimize pH variations and effluent volume and save water, chemicals and energy, *Dresch et al [40]*.

Ultrafiltration

Ultrafiltration (UF) is defined as a membrane filtration process that does not reject ions, Figure 3.5, with UF rejecting solutes above 1000 Dalton (molecular weight). Due to the larger pore size in the membrane, UF typically requires a much lower differential operating pressure: 0.7 to 6.9 bar. UF removes larger organics, colloids, bacteria and pyrogens whilst allowing most ions and small organics such as sucrose to permeate the porous structure.

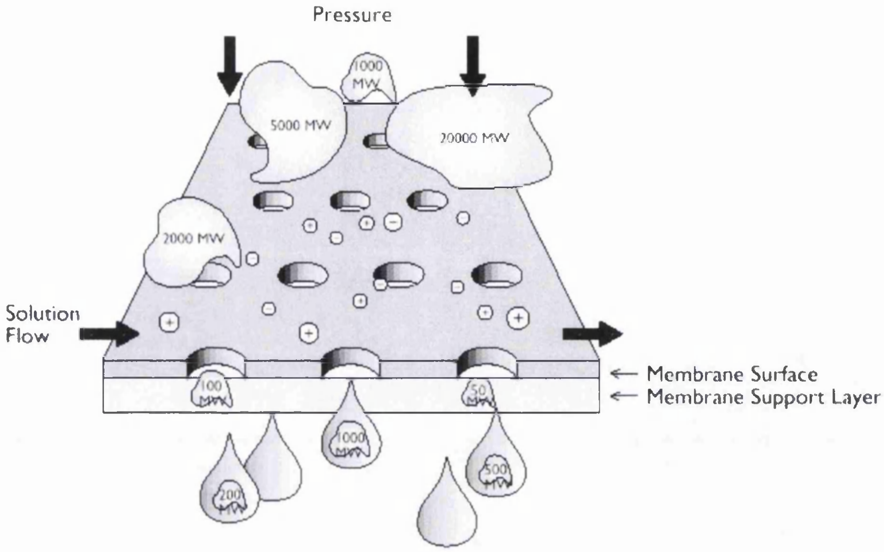


Figure 3-5 Principle of Ultrafiltration showing typical rejection of solutes *Osmonics [41]*

It is because of these properties that UF has found many varied and wide applications. Drinking water quality and the control of *Cryptosporidium* and *Giarda* cysts, which have a high resistance to commonly used disinfection techniques, e.g. chlorine and UV light, has fuelled the use of absolute filters to effectively remove 99.99% of *Cryptosporidium* sized particles, *Knops and Franklin [42]*.

Many applications for UF exist in the biotechnology area where typically the higher value of the recovered product can justify the initial high capital costs of the membrane plant. Some uses are:

- UF of molasses to effectively desalt and thus enhance fermentation, *Ryan and Johnson* [43]
- Clarification of wine to improve presentation, *Fernandes et al* [44]

- Recovery of proteins and enzymes using UF has been used extensively, *Noordman et al [45]*, with the advantages of UF being highlighted as far back as 1975, *Crocco [46]*.
- Recent environmental concerns regarding the disposal of unrecoverable enzymes from surimi wastewaters has led to further research into maximising recovery of catheptic proteases so as to reduce pollution, *DeWitt and Morrissey* [47].
- The ability of UF to allow the passage of small organics, like sucrose has led to much interest in the sugar refining industry, *Bhattacharya et al [48], Hinkova et al [49] and Gekas et al* [50]

The recovery of product from waste streams and maximising yields is the consistent theme behind the use of UF in the sugar industry.

The integration of membranes into a unit operation to produce a hybrid process has seen much rapid development, examples of this approach is in the use of membrane bioreactors, MBR. They have been extensively developed for the treatment of water and wastewater, *Bohdziewicz et al [51], Cheng Wen et al [52], and Defrance and Jaffrin [53]*, due to the ability of the membrane to maximise the use of enzyme and reduce the footprint of the complete process plant. The development of processes to remove metal ions from waters using a combination of UF and chemical techniques, *Vieira et al [54]*, in an area where NF or RO is normally employed, is growing due to the lower operating costs of UF. The use of selective precipitation techniques will also allow the removal of a potentially more valuable "waste", *Fletcher and Akgerman [55],* from a stream to recover a "product". By combining the metal ion using coagulation-flocculation or addition of polymers, the resulting larger body can be more easily removed using UF, *Pyung-kyu Park et al [56]*.

Microfiltration

Microfiltration (MF) membranes are filters typically rated in the 0.1- to 3.0-micron range see Figure 3.6. Available in polymer, metal and ceramic membrane discs, sheets, fibres, tubes or pleated cartridge filters, MF is also available in crossflow configurations with typical operating differential pressures of 0.3 to 3 bar. Increasing use is now being made in the pre-treatment of RO systems, *Chakravorty and Layson [57]*, as traditional mixed media filters, i.e. sand, cannot remove particles down to the same size range as MF with the same consistent reliability. Silt density Index (SDI) studies at Margam C Demin plant at Port Talbot highlighted the inefficiency of the media filters used after the initial coagulation-sludge blanket treatment. This inefficiency resulted in extended backwashing runs on the ion exchange beds as the ion exchange media was acting as an additional filtration stage. The use of MF membranes as a replacement to the media beds would reduce water and cleaning-in-place costs due to their reliability to remove particulates from aqueous streams as highlighted by *Chakravorty and Layson [57]*.

The ability of MF to produce a quality of permeate regardless of the feed concentration is an attractive reason to use MF, *Ebrahim et al [58]*. The main aspects of capital cost reduction in a RO system are in reduced size of chemical dosing systems, elimination of fine pre-RO filter cartridges with further savings in operating costs by extending the life of the RO membrane, less RO system downtime, less maintenance of high pressure system, lower chemical consumption and reduced man power to run MF plant.

MF has many other applications for water treatment and compliments membrane filtration processes other than RO. MF is used as a pre-treatment to further processing by UF in the dairy industry to remove fat and bacteria, clarification of whey, filtration of fermentation broths, especially in the production of lager to remove fermentation yeast.

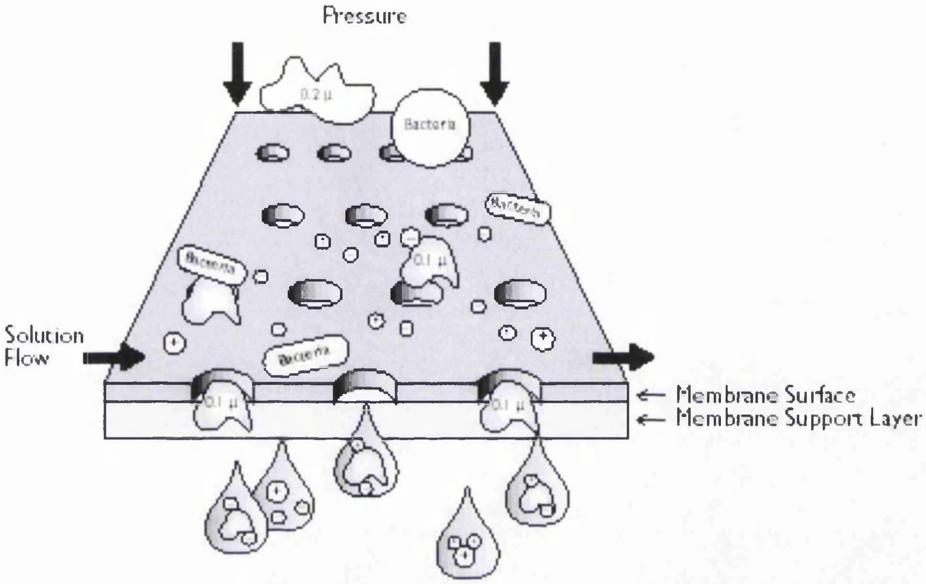


Figure 3-6 Principle of Microfiltration showing typical rejection of solutes, *Osmonics.*

Surface water treatment is a growth area for membrane filtration as the demand placed on traditional supplies increases. *Hofman et al* [59] studied the removal of phosphate and iron from seepage and surface water by MF and compared the costs to previous work done using UF. By combining MF with an effective chemical pre-treatment to form phosphate and iron complexes, they found that the MF system produced a good quality permeate with regards the key parameters of phosphate and iron removal whilst operating at a lower cost to UF by reduction in operating pressure and cleaning chemicals.

3.4 Prediction of Membrane Performance

It is currently not possible to present an equation, or set of equations, that allows the prediction from first principles of the membrane permeation rate and solute rejection for a given real separation.

General Membrane Equation

The general membrane equation, Equation One, is an attempt to state the factors which may be important in determining the membrane permeation rate for pressure-driven processes and is presented below, taken from *Coulson and Richardson [60]*.

Equation 1

$$J = \frac{|\Delta P| - |\Delta \Pi|}{(R_m + R_c + R_f^{'})\mu}$$

Where:

J membrane permeation rate (flux expressed as volumetric rate per unit area),

ΔP pressure difference applied across the membrane (transmembrane pressure), units of pressure.

$\Delta \Pi$ is the difference in osmotic pressure across the membrane,

R_m is the resistance of the membrane,

R_c is the resistance of layers deposited on the membrane

R_f' is the resistance of the film layer

μ is the viscosity of the fluid being filtered

If the membrane is only exposed to pure solvent, e.g. water, then the equation reduces to the Carman-Kozeny equation, Equation 2 –*Carmen [61]*:

Equation 2

$$J = \frac{|\Delta P|}{R_m \mu}$$

Calculation of the pure water fluxes is useful for characterising and benchmarking new membranes thus allowing an assessment to be made of the effectiveness of cleaning procedures on the membrane. The limitation of the general membrane equation is that the resistances are not readily calculable but instead estimated from flow data and a value assigned to each resistance based upon operating experience of similar solutions.

Concentration Polarisation

Separation of the solute and solvent takes place at the surface of the membrane. Here the solvent is allowed to pass through the membrane and the solute is retained. Very near the surface of the membrane, the local concentration of the solute increases and a concentration profile is established within the boundary film generated by the specific hydrodynamic conditions, see Figure 3.7. This difference in concentration will drive the solute back into the bulk solution according to Fick's Law of diffusion.

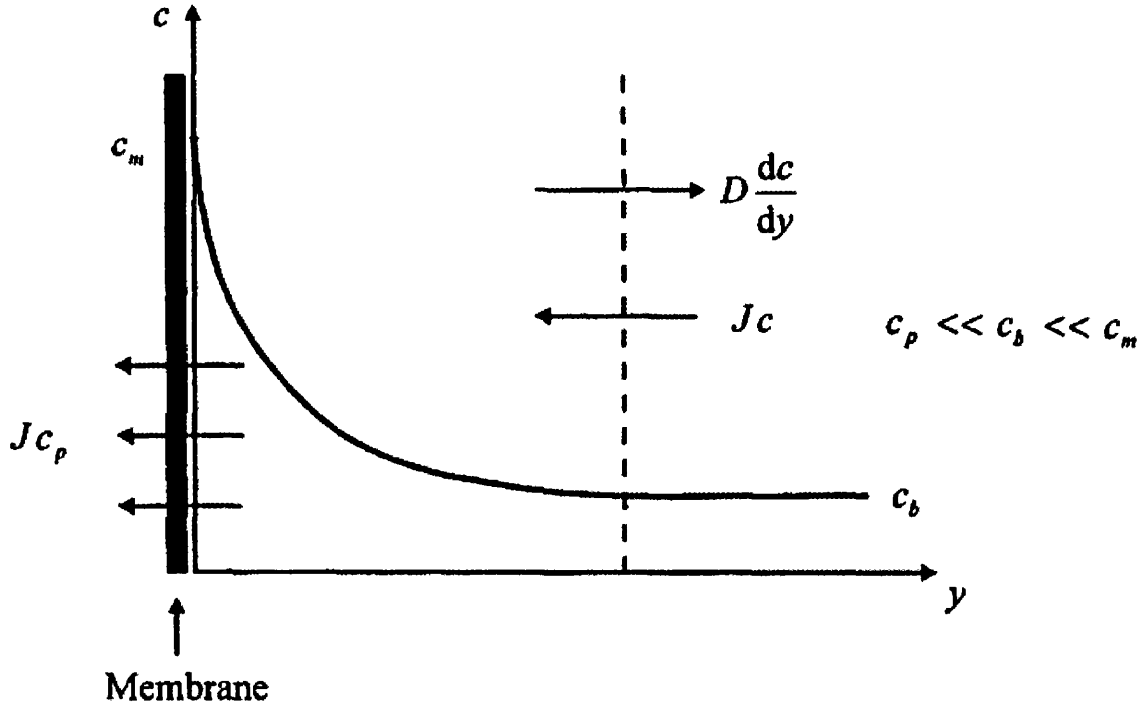


Figure 3-7 Concentration polarisation at a membrane surface

By conducting a mass balance above the surface of the membrane with the assumptions that:

1. Concentration gradients parallel to the membrane are negligible compared to the concentration gradients orthogonal to the membrane.
2. Solvent and solute densities are similar.
3. The diffusion coefficient is constant.

At steady-state, the rate of back diffusion will be equal to the rate of removal of solute minus the rate of solute leakage through the membrane,

Equation 3

$$Jc = D\frac{dc}{dy} + Jc_p$$

Where:

c and c_p are solute concentrations in the boundary layer and permeate respectively

D is the diffusion coefficient of the solute in the solvent.

By integration of equation 3 using the boundary conditions:

$c(y = \delta) = c_b$ $\qquad$ $c(y = 0) = c_m$

gives the following film model relationship:

Equation 4

$$J = k_s \ln\left(\frac{c_m - c_p}{c_b - c_p}\right)$$

Where $k_s = D/\delta$, the overall mass transfer coefficient of the solute in the boundary layer, and c_m is the concentration at the membrane surface.

The overall mass transfer coefficient is usually obtained from correlations based on the Sherwood and Schmidt dimensionless numbers, which are able to take into account the hydrodynamic conditions. Although the above theory is based upon ultrafiltration, it can also be widely applied to microfiltration.

Gel Polarisation Model

By the plotting of flux against applied pressure, researchers found that a point is reached where a further increase in pressure results in little or no increase in flux. It was therefore suggested that as the concentration at the membrane surface reaches its solubility limit, the solute precipitates and forms gel like layer on the surface of the membrane. In the filtration of colloidal particles, this layer is thought to resemble a layer of close packed spheres *Porter* [62]. This constant gel layer concentration is quickly reached and is thought to be independent of the membrane characteristics, bulk solution concentration, fluid flow conditions and applied pressure.

By increasing the applied pressure, more solute is brought to the surface thus increasing the layer's thickness thereby reducing the flux back to the original level. For 100% solute rejection (cp = 0) the previous equation, (4) can be written in the form:

Equation 5

$$J_{\lim} = k_s \ln\left(\frac{c_g}{c_b}\right)$$

Where:

c_g constant gel layer concentration
$J_{\lim}$ is the limiting flux

Many workers have obtained experimental results for the limiting flux, which give strong support to the gel-polarisation model, namely:

J_{lim} is independent of applied pressure

J_{lim} is semi-logarithmically related to c_b

J_{lim} approaches zero at a limiting bulk concentration $c_{b(lim)}$ which is equal the gel concentration c_g (or the cake-concentration in the case of colloidal dispersions)

J_{lim} may be modified by factors that alter the overall mass transfer coefficient k_s.

Although useful for interpretation of ultrafiltration, several limitations exist that cannot be explained by the theory. By using bulk concentrations equal to the concentration predicted at the membrane surface, the resultant permeate flux was not equal to zero as predicted by the model. The use of identical solutions and hydrodynamic conditions when using membranes of different permeability produced different values of the limiting flux, implying that the membrane properties had an influence. In the filtration of colloidal particles, fluxes have been reported several times higher than predicted by the gel polarisation model and conventional mass transfer coefficients. This has become known as the flux paradox for colloidal suspensions.

Fouling

A limitation to the more general use of membranes is membrane fouling. It is defined by *Mulhern* [63] as:

"Fouling is a broad, generic term used to identify a multitude of time dependant phenomena, which singly or in combination, impact membrane performance."

Fouling results in a continuous decline in membrane permeation rate, an increased rejection of low molecular weight solutes and eventually blocking of flow channels. On start up of membrane processes, the permeation rate will normally decline rapidly after a few minutes and then more gradually throughout processing. The extent of membrane fouling depends on the nature of the membrane used and on the properties of the process feed.

Fouling of ultrafiltration and microfiltration membranes is encountered in all areas of filtration and treatment of colloidal suspensions across all industries [*65-71*]. The substantial decrease in the flux rate may or may not be recovered by subsequent cleaning of the filter. Depending upon the nature of the fouling, i.e. reversible or irreversible fouling, cleaning methods need to be implemented to return the permeate flux to a level that allows continued productive use of the membrane. Attempts have been made to prevent the fouling of the membrane by techniques like surface modification of the membrane, *Cohen* [72] by the addition of polymers to the initial membrane surface, physical adsorption of non-ionic surfactants onto the surfaces of hydrophilic polymeric membranes to improve oil rejection, *Anderseon* [73] and producing corrugated membranes [74] to name a few. These techniques have brought about improvements in extending the operational flux but have not totally removed the need for cleaning.

The three main mechanisms of flux decline in the ultrafiltration of colloidal species are standard pore blocking, pore blocking and cake build-up *Davies and Tracey* [75]. They can be described by the following equations:

Equation 6 Standard Pore Blocking

$$R_m + R_i = R_m(1 + K_{SPB}Q_o t)^2$$

Equation 7 Pore Blocking

$$R_m + R_i = R_m \exp(K_{PB}t)$$

Equation 8 Cake build-up

$$R_T = R_m(1 + 4K_{CB}Q_o^2 t)^{1/2}$$

Where: R_m is resistance of the membrane

R_i is resistance due to internal fouling of the membrane

R_T total membrane resistance

K_{SPB}, K_{PB} and K_{CB} are constants for standard pore blocking, pore blocking and cake build-up

Q_o is the initial permeate volumetric flow

t is time.

In standard pore blocking, flux decline is due to the gradual constriction of pores while the available number of pores remains constant. The pore-blocking model assumes that the pore size remains constant but that the number of pores decreases with time due to pore plugging. For the cake filtration model, internal membrane fouling due to pore plugging does not occur and only the resistance due to the build up of cake occurs.

Cleaning

Cleaning of the membrane is an essential part of the successful operation of a membrane process and requires careful consideration for the extended lifetime of the plant. Membrane cleaning procedures prevent continuous operation of the plant causing downtime and consume reagents to restore membrane flux that can even cause degradation to the membrane, as well as the system components, e.g. pump, pipe work, fittings, due to there often corrosive nature. Non-chemical cleaning methods have been used to reduce the amount of chemicals consumed, these are primarily back flushing techniques using air or permeate *[76-78]*, ultrasonic methods [*79-80*], and variation in the flow dynamics like high shear rates [*81-83*].

Biological fouling is an operational term, defined by *Flemming* [84], as applied to when the effects of bio-films exceed a certain threshold, or tolerance level, which is individually set for different systems. It is not directly caused by the filtration of a specific solute, but due to the nature of the system, the warm and wet conditions lend themselves to growth of organisms. It has also been identified as a difficult problem to overcome and eradication from the membrane requires aggressive measures. The development of pH and chlorine resistant membranes has allowed biological growth to be controlled by chemical sterilisation.

The first means of control is therefore careful choice of membrane type via selection of suitable materials that minimise the growth of fouling layers by physiochemical means. Secondly, a module design which provides suitable hydrodynamic conditions to further minimise the inevitable growth of a fouling layer for the particular application in question should be chosen. These principles often have a positive effect of reducing the solute fouling layer. A thorough overview of techniques to improve microfiltration is presented by *Wakeman and Williams [85]*, although dealing primarily with the fouling caused by protein deposition on MF membranes; many of the techniques apply to all fouling solutes on MF as well as UF membranes.

The cleaning of the membranes used in this study was carried out using a method similar to one suggested by *Muller et al [86]* of an alkaline-acid rinse with an additional alkaline rinse only used if the PWF was not in the value range expected for that membrane.

3.4.1 Membrane –Solute interactions

As previously stated, a major limitation of membrane filtration is fouling. The interaction between the membrane material and the solute is an important one as this is the main interface that determines permeability of the solute and operational time of the membrane via its effect on fouling. The following table, Table 3.2, summarises the effect of membrane – solute interactions in flux decline as presented by *Musale and Kulkami [87]*:

Mechanism of Flux decline	**Membrane parameter**
Concentration polarisation at membrane surface	Module hydrodynamics
Membrane compaction	Membrane morphology, polymer strength
Pore narrowing through solute-adsorption	Membrane-solute interactions, Surface roughness
Pore blocking through solute deposition	Membrane-solute interactions Pore size and tortuosity
Solute Adsorption/deposition at membrane surface	Membrane-solute interactions Module hydrodynamics Surface roughness

Table 3-2 Role of Membrane Characteristics in Flux Decline ***Musale and Kulkami [87]***

The paper also covers the membrane surface characteristics, highlighting the importance of hydrophilicity on UF. In the paper they cite several references where higher permeate fluxes have been achieved when the membrane surface is more hydrophilic although much of the discussion is based on the filtration of protein solutions. Surface roughness was discussed and how this may affect concentration polarisation / fouling through either a change in surface free energy which could increase adhesion of surface-active molecules or liquid stagnation in the surface depression resulting in high local concentration polarisation at the pore entrances reducing flux and increasing fouling. Increased pore size leads to an increase in flux both of pure water and process streams but when similar size solutes are being filtered when compared to the pores size, ingress of solutes into the membrane can occur as well as pore blocking / plugging.

3.5 Oil-in-water (O/W) Emulsions

Background and Definition

An emulsion is a generic term used to describe an essentially homogenous system where a substance is dispersed equally in a medium but is discrete from this medium. Many examples exist and some of the more common ones are milk, aerosols and engine emulsions. Primarily this work is concerned with oil in water emulsions used in cold mill rolling operations and is an example of a liquid in liquid emulsion. Dispersions of liquids in liquids display many of the properties of dispersions of solids in liquids but there are also some different phenomena displayed.

One important property is that the suspended droplet can change size by coalescing with another droplet. This is dominant in a system that is made up of insoluble components. To prevent this system separating and forming distinct layers, a substance is used that is able to act as a barrier to coalescence. The emulsion is eventually expected to separate into the two separate components, as this is the state of lowest free energy. Substances can be added that delay the separation and the emulsion can remain stable for long periods of time, up to several months. This is of particular use in the paints and food industry, as shelf life becomes an important factor.

Most emulsions used in industry are proprietary in nature and the exact composition is not available but in general they contain ionic and non-ionic surfactants and biocides. During use they pick up metal ions and other contaminants that then degrade the emulsion properties rendering it unsuitable for use. This used emulsion then needs to be replaced with fresh emulsion and the waste emulsion treated and disposed of. Disposal of this waste is an important area as tighter laws governing discharges to sea and sewers are drawn up. Oil and grease disposal for Port Talbot are continually monitored.

Current treatment methods, using chemical and flocculation techniques, produce two waste streams, a watery sludge and treated water. Both of these streams are waste and are not reused in any way. The sludge has extremely high water content and relatively low oil content so cannot be burned, with the wastewater stream sent to a sump and disposed to sea. The quality of this stream is very variable and is not tested by chemical means for oil and grease but a visual inspection is made of the quality. It is in this area where membranes can begin to reduce waste products and actually produce water of a quality that is of further use within the works.

Emulsions can be termed either macro or micro emulsions depending upon their size. Macro emulsions are generally classified as being greater then 0.1-micron diameter droplets and micro emulsions as less than 0.1 micron. The emulsion used in the cold rolling process is of a macro emulsion type and a droplet size distribution using low angle laser light scattering can be seen in Figure11. This is from a spent emulsion and the spread in droplet size can be explained due to the emulsion having been used in a rolling process and other shear events like pumping. The forces exerted on it have in some cases caused some coalescing of droplets by squeezing the droplets together and also possibly the formation of smaller droplets by mechanically flattening and breaking the emulsion, resulting in this spread of droplet size.

Membrane Treatment of Emulsions

In the membrane treatment of oil-in-water emulsions, the pressurised feed stream is passed across the membrane with the membrane excluding the oil droplets based primarily on size. Although analogous to the separation of solid liquid systems, the membrane treatment of oil-in-water emulsions offers additional phenomena due to the deformable nature of the droplets. A good introduction to the problem of membrane filtration of emulsions is presented by *Fane et al [88]*. Fane *et al* introduce the fundamental aspects involved and report results of various membranes on the filtration of two fresh emulsions.

Membranes have been shown to be able to concentrate oil emulsions up to 60% oil, *[24]*. In 1998, it was reported by *[24]* that over 3000 commercial membrane plants were in use for the processing of oily wastewaters worldwide. The authors offer some guidelines on the use of membranes compared to conventional treatment technology, highlighting some real examples of systems in the speciality chemicals, metal fabrication and the automotive industry.

The use of membranes has also been reported where the membrane is not used a filter but as a coalescing media for the oil droplets, *Hlawacek [89]*. It was proposed that as the oil droplet is squeezed through the membrane pore, the surfactant film surrounding the droplet is removed by the shear effect and friction at the pore walls. The permeate is then allowed to settle for 2 hours, allowing the phases to separate. Energy costs are kept at minimum due to the operation of the membrane at lower applied pressures but a relatively high permeate oil concentration of between 50 –100 ppm, after settling, is reported. Although this compared favourably to the concentration of 30000 ppm in the original emulsion, the permeate phase still requires further settling as the increased droplet sizes need to be separated.

Synthetic Emulsions

Work by *Nazzal and Wiesner [90]* using ceramic microfiltration membranes on a simulated 500-ppm chlorobenzene oil-in-water emulsion looked into the effect of pore size and applied transmembrane pressure upon the passage of oil droplets through the membrane. They reported that due to the deformability of the oil droplets, the transmembrane pressure relative to the membrane pore size and size distribution of oil drops in the feed is likely to be a critical operating variable as are membrane composition and solution chemistry. The comparison between the predicted theoretical pressure required for the passage of oil through the membrane and actual produced results that suggested that the solution being filtered was not exhibiting ideal behaviour.

"Real" Emulsions

It is the combination of both oil droplets and metal ions that cause problems when dealing with effluents from the work place that has prompted work using combinations of different treatment technologies to produce permeates that meet standards regarding metal ion concentration as well as COD. *Lin and Lan [91]* worked with an effluent from the cable and wire industry which contained a high oil content, upto 3%, and copper ion concentrations of around 300 mg/l. By using a combination of hydrophilic spiral wound polyether sulfone UF at a pressure of 0.24MPa and spiral wound polyamide RO membranes at 0.8MPa, they were able to produce a permeate that allowed direct discharge to drain or can be considered for reuse. After UF, 92.9% removal of COD and 89.5% of copper was further increased via RO to 99.9% COD and 99.8% copper.

The use of UF as pre-treatment for the RO stage also sufficiently removed the presence of bacteria to a level that allowed operation of RO without the imminent threat of bio slimes and other bacteriological fouling associated with the use of RO membranes and their typically higher operating temperatures.

A similar study by *Karakulski et al [92]* using self-fabricated tubular polyvinyl chloride (PVC), polyacrylonitrile (PAN) and cellulose acetate (CA) UF membranes at 1.5 bar, on a waste emulsion from a shore side settling tank in Szczecin-Swinoujscie harbour, followed by RO at 35 bar, using CA RO membranes supplied by PCI (UK). COD removal varied from 72.5% for the PVC membrane, 78% for the PAN and 89.8% for the CA, with very little removal of the TDS, greatest % removal was PAN 8.6%. Further treatment by the RO module increased COD removal to 93.2% and TDS removal to 95.2%. UF flux values for the oil filtration ranged from 48-55 L m^{-2} h^{-1} for the PAN membrane, 28-35 L m^{-2} h^{-1} for the PAN membrane and 18-25 L m^{-2} h^{-1} for the CA.

The resulting permeates produced by the combined treatment processes are similar in both studies and is of a high quality. It is apparent that that the higher operating pressures of the RO stage would significantly increase the operating costs of the process and that paths would need to be explored that allow the permeate to be reused as a process stream to offset these costs. These two studies highlight that technology exists to produce consistently high quality permeate, albeit at a high cost when compared to normal methods of producing similar quality process waters from quality water sources. Disposal of the concentrated oil emulsion was not mentioned within the papers but combined with reuse of the permeate, methods of recovering costs via the waste emulsion, possibly by selling the oil to companies that can recover it for its reuse or possible fuel source, need to be investigated to make the processes economically viable when combined treatment schemes are to be employed.

Ceramic membranes are used extensively in the treatment of emulsions. *Wang et al [93]* present results of a pilot study of the treatment of waste rolling emulsions were reported. In the study, zirconia microfiltration membranes were used to treat the waste produced by a Chinese rolling mill. The authors investigated the use of a pre-treatment agent as an aid to filtration and the reliability of the process to reject oil. The membranes used had 0.1-0.2 micron pore size with an effective module membrane area of 0.22 m^2 and two modules were used. Initial filtration results looked at two materials, zirconia and alumina, to determine the optimum membrane for more extensive testing. The zirconia membrane produced higher specific flux values so was adopted in the further trials. A possible reason for this given by the authors was due to the higher surface energy of the zirconia membrane and this subsequent effect upon the fouling mechanisms. This was not proved in the paper.

The paper describes the effect of transmembrane pressure, TMP, and crossflow velocity, CFV, on flux. For a given velocity with an increase in pressure, the flux also initially increases as the driving force is greater. A point will be reached when the subsequent increase in pressure will produce a decrease in flux. This is due to the deformation of the oil droplet and the entering of the droplet into the membrane pores with subsequent fouling. At the higher velocities it was observed from the results of *Wang et al* that the pressure required to produce a negative impact on flux was lower as velocity was increased.

This is an interesting observation as at higher velocities, the time spent by the emulsion in the membrane module is less so you would expect higher pressures before the degradation in flux. A possible reason for this is due to the emulsion being exposed to a cleaner membrane at the higher velocities due to the more scouring nature of the flow pattern. This would produce a thinner gel layer on the surface so producing less resistance to the perpendicular pressure force and allowing the droplet to enter the pore and foul due to a possible pore blocking mechanism. The ability of the membrane to be cleaned by "normal" cleaning procedures would need to be investigated as this could produce possible "permanent" fouling and the need for a stronger cleaner that can enter the pores and remove/dissolve the oil entrained in the pore. At low pressure, 0.1 Mpa, the flux increases linearly with CFV as the pressure force is not great enough to squeeze the oil droplet through the membrane pore.

The influence of feed temperature is also reported. For short term runs, it was reported that the flux increases linearly with temperature as expected due to the reliance of flux upon the viscosity of the feed solution. For the longer-term runs, the authors reported that flux dropped off substantially. This is due to the greater time allowed for the oil droplets to "attack" the membrane pores and foul them. In the short-term runs the time was not long enough for the oil to enter the pores before the experiment was terminated and the membrane cleaned. Although an increase in flux is seen with temperature, the energy for this temperature increase has to come from somewhere.

A balance between the different energy streams is required so that the membrane operates at maximum performance. In the case of emulsions, a temperature rise inevitably results in problems due to the decrease in viscosity of both the oil and water. Less resistance to the oil entering pores is seen and results in fouling. This fouling is generally more severe than "normal" fouling by gel layer formation as the cleaning regime needs to take into account the blocked pore. A cleaner is required that can enter the pore and effectively remove the foulant.

3.6 Solid-solvent Separation

The separation of small and possibly highly charged solids from a solvent such as water, is another area of interest for using membranes due to traditional methods being costly or cannot reliably produce a quality of effluent that can be reused / recycled.

General Considerations

The separation of solids from an aqueous stream is an area that has seen a lot of research over the last 30 years. Formation of a cake layer during the filtration of these streams results in flux decline and work has been carried out to model this layer *[94-98]*. Much of this work has concentrated on the use of monodisperse silica latex colloids and / or the use of small scale stirred cells or dead end experiments. The results reported are generally in agreement with the theories that each researcher bases the development of the models on. The use of these ideal conditions allow the development and reproducibility of modelling work but are of limited use when filtering on much larger scales where the size distribution of particles is variable.

Development of models and theories based on polydispersity has been approached, requiring more sophistication to account for the extra effects, *[99-100]*. Sieving effects can take place that allow smaller particles to be predominantly deposited on the membrane surface. Both *[98] and [99]* have reported that the smaller particles predominantly form the cake layer and that the larger diameters are present in the bulk. They calculate the cake resistance and hydrodynamic effects separately to determine the overall influence of the polydispersity.

Surface charge, on both membrane and particles, has an influence on the flux rate and therefore fouling rate. A thorough review of these effects from a particle-particle perspective is covered in *Huisman et al [101]* with the general observation that permeate fluxes have been reported to increase as the zeta-potential of the feed suspension particles increases. This increase is explained by high values of zeta potential increasing inter-particle repulsion and the formation of looser layers and more permeable cakes. A study of the influence of the membrane surface zeta potential on the critical flux, *Huisman et al [102]*, i.e. the level at which minimal fouling occurs, concluded that neither the zeta potential of the membrane or of the particles influenced the observed critical flux. The dependence of zeta potential on pH as well as conductivity and ion valencey in the solution needs to be considered.

Backtransport of particles

The concentrated layer of particulates builds up due to the convective fluid flow towards the membrane. The thickness of the fouling layer will increase until the cross-flow induces a shear stress that is large enough to re-entrain particles in the outer layer, i.e. those that are furthest away from the membrane surface. The flow of permeate takes particles towards the membrane surface whilst the cross flow of the feed takes particles back into the bulk. When a filtration has reached steady state, these forces are balanced.

Many different mechanisms have been put forward to explain the movement of particles back into bulk. Which mechanism is dominant during the filtration depends largely on particle size with physiochemical interactions also having an influence. For particles less than 0.5 microns in diameter, Brownian diffusion is the dominant mechanism, *Blatt et al [103]*, for particles between 0.5 and 20 microns in diameter, shear induced diffusion, *Davies and Romero [104]* is the main consideration and for particles greater than 20 microns in diameter, inertial lift, *Drew et al [105]* is considered dominant. In the main area of membrane filtration of colloidal suspensions, the particle diameter is between 0.5 and 20 microns, so shear induced diffusion is most likely. A review of these mechanisms is given by *Davies [106]*.

Due to the nature of cross flow filtration, turbulence will have an effect. By changing the flow field via a change in bulk flow rate, the shear stress on the walls and surface of the built up fouling layer is changed. When a shear force is applied across a layer of particles, as in a fouling layer, the particles are able to move over one another forming a layer that is more loosely packed. This resulting migration of particles can be described by an effective diffusion coefficient which is a factor of particle radius, wall shear stress, viscosity and particle volume fraction, *Leighton and Acrivos [107]*.

3.7 Aims and Objectives of work

Due to the large distributed nature of the water / effluent system within the steelworks, large end of pipe treatment methods do not offer the flexibility to deal with varied effluents to meet future demands on both discharge consents and recycling guidelines / best practice. The continued drop in costs of membrane processes and their ability to treat traditionally difficult and expensive effluents warrants further investigation into their use in the steel industry.

The majority of previous work is based around small-scale prescribed model effluents that concentrate mainly on the science of membrane water treatment processes with little work being available on real systems especially in the steel making area. To address these shortcomings, the following aims for the project were formulated:

1. Identify suitable effluent streams that have the potential to be treated using membrane processes.

2. Investigate the ability of membrane processes to treat these streams and produce a quality of permeate that can be either reused or as a feed for further treatment, typically < 10 PPM of oil and <10 PPM of suspended solids.
3. Produce specific flux and cleaning data for the selected membranes / feeds.
4. Using experimental data, prepare a cost benefit analysis of membrane processing to produce an estimated current price for 1 m^3 of treated effluent.

To meet these aims the following work plan was devised:

- Spend time with the works Energy Department and gain an understanding of the day-to-day issues that affect the water treatment system.
- Design and construct a pilot scale membrane water treatment plant that is flexible enough to incorporate different types of commercially available membranes over a range of operating conditions.
- Conduct experiments on the selected streams using a variety of membranes and determine the important operating parameters.

4 Materials and Methods

4.1 Experimental apparatus

Having selected the types of effluent that were to be investigated, certain criteria was identified which would impact on the design of the experimental apparatus. Based on the types of effluent, it was decided that the operating pressure of the rig was generally to be less than 5 bar. To make the rig as realistic as possible, it was important that the rig was able to accommodate full size membrane models that are used in large commercial operations.

Literature was reviewed from several membrane companies; Koch Membrane Systems were contacted for details of their systems. Several Koch built pilot rigs were quoted for but not one was able to other much flexibility in housing different module types. Although a rig was not going to be ordered from Koch, the details and information provided on their membranes met the criteria for the types of separation. To this end, it was decided that a rig design was to be drawn up based on using Koch tubular and hollow fibre membrane modules and equipment manufactures contacted to provide quotes and advice for instrumentation and pumps.

Due to the wide range of operating conditions that the rig could be expected to operate under, the material of construction was 316 L stainless steel. The normal operating flow rates of the modules recommended by Koch varied from 2 m^3 / h and 4 m^3 / h. To be able to operate at these flows and the pressure range of the membrane, 2 – 4 bar, a vertical multistage pump with motor speed control via an inverter was used. This converted the single phase to a three-phase supply to the pump motor. The pump used is a widely available model within the water treatment area although the motor was up rated to ensure that the flows could be provided at the pressure range expected.

To ensure that the instrumentation used was capable of producing accurate readings, pressure, temperature and flow measurement was made using equipment widely used within Port Talbot. This meant that the instruments were already proved in a harsh environment on similar effluents, calibrated regularly and that they could be programmed using existing equipment within the Energy department.

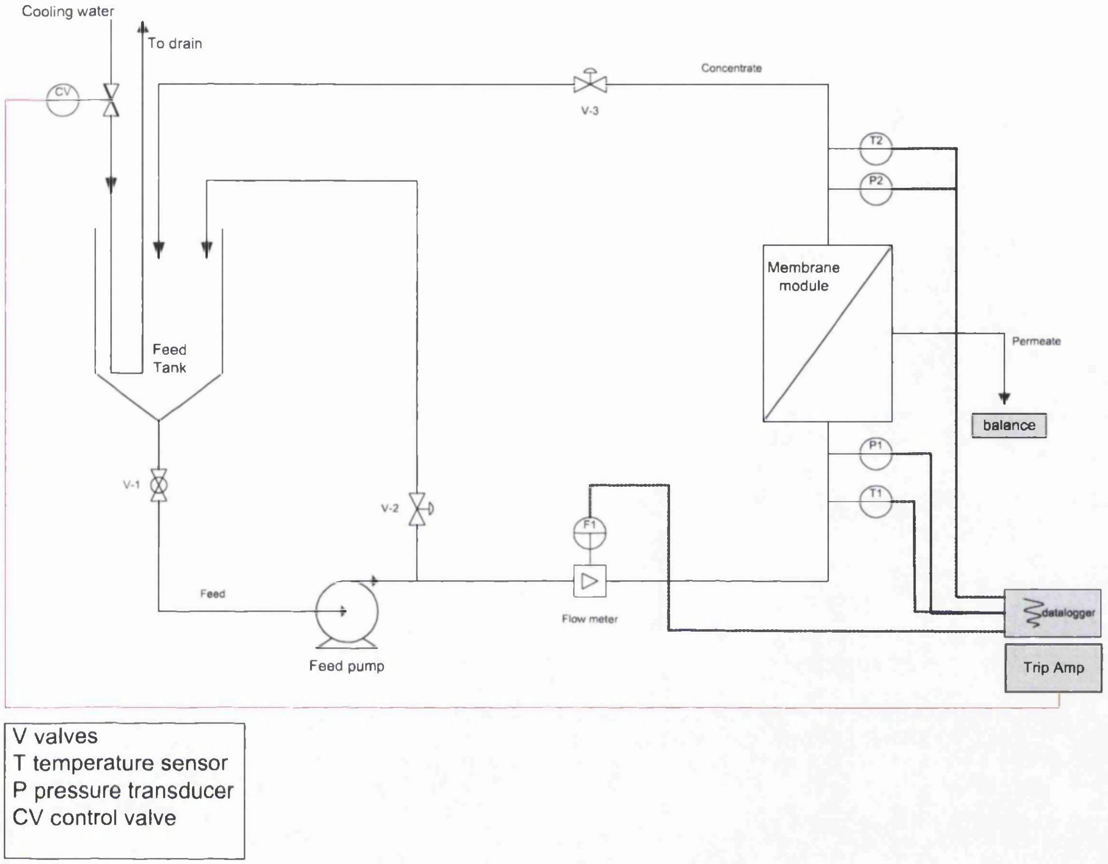
To allow for accurate reading of the two different types of effluent, a vortex flow meter was chosen from Fisher Rosemount that could be programmed to operate in narrow ranges of flow to increase precision if required and was covered by quality assurances from the company. Over the range of operating flows used, the deviation of flow measured by the Fisher flow meter was certified between ± 0.65% error, with the actual certificate showing to be within ± 0.11% error of the flow. In the case of the temperature measurement, the reading accuracy was to be ±0.15 of a degree and for the pressure sensors, ± 0.001 bar. This ensured that the readings taken from each instrument was as accurate as was reasonably possible.

Based on the above rationale, a membrane pilot plant, Figure 4.1, was constructed. The rig can house both hollow fibre and tubular membranes, operate up to a pressure of eight bar and deliver a maximum flow rate of 8 m^3 / h. The feed tank has a maximum volume of 165 litres and the wetted parts are constructed from 316L stainless steel; pipe work was 1.5-inch dairy tubing with the box-supporting frame made from 304 stainless steel. The rig was mounted on lockable casters to enable easy movement and stable operation. All the pipe work was connected using tri-clover clamps to allow for quick membrane fitting and access to the instrumentation. The feed tank also contains stainless steel cooling coils, with the cooling water flow rate automatically controlled using an on/off solenoid valve and a trip amp, (Moores Industries SPA) in conjunction with online temperature measurement.

A schematic of the cross flow membrane pilot plant is shown in Figure 4.2. A vertical multistage pump (Lowara, SV408T22T ITT Industries, Goulds Pumps Ltd, Axminster, Devon) supplies the driving force for feed circulation and operating pressure. An initial pressure can be set using the pump's inverter (Hydrovar, Goulds Pumps) and the flow rate then controlled using V3 (full-bore diaphragm valve) until the desired conditions are met. Two pressure transducers (Kamstrup FlexBar, Aabyhoej, Denmark) are used to monitor the inlet and outlet pressures of the module and a third was available to measure pressure on the permeate side where possible. A vortex flow meter (Fisher-Rosemount Model 8800AF010SA1N1P1I1, Heath Place, Bognor Regis, UK) was used to measure the feed flow rate to the membrane. Temperature sensors (Kamstrup R /T assembly Flextop head mounted transmitter, Aabyhoej, Denmark) are also in place on either side of the membrane and this fed back to a cooling system so as to maintain an average operating temperature of 25°C ±0.5 °C.

Figure 4-1 Pilot Rig showing PS Hollow fibre Membrane

Figure 4-2 Process Schematic of Pilot Rig



All the instruments used are loop powered using din rail power supplies (Kamstrup, Aabyhoej, Denmark) and generate a 4-20 mA signal which was first sent to a remote display (Kamstrup FlexView panel Mounting programmable, Aabyhoej, Denmark) mounted on the control panel and then recorded using a process datalogger (ACR Systems Inc. Smart Reader Plus 7, Surry, B.C. Canada). The permeate flow was measured gravimetrically by an electronic balance reading to one decimal places.

Equipment Schedule

Item

Variable speed pump:	Lowara SV408T22T Pressure range 0-8 bar Volumetric flow-rate 0-8000 l/hr
Piping and fittings:	1.5-inch dairy tubing 316L stainless steel
Frame:	100mm boxed 304 stainless steel on four casters (two lockable)

Instrumentation:

Vortex flow-meter	Fisher-Rosemount Model 8800AF010SA1N1P1I1
Pressure transducers X 3:	Kamstrup–1–16bar programmable pressure transmitters
Thermocouples X 2:	0-100 °C Kamstrup R /T assembly
Instrument Displays X 6:	Kamstrup programmable displays, Cables, clips, box
Datalogger:	ACR info-loggers SRP 7 channel process datalogger Toshiba Satellite 4030CDT

4.2 Membrane Modules

The apparatus can accommodate two basic types of membrane, a vertically mounted module up to 0.91 meters long and a horizontally mounted module up to 1.52 meters long. Two basic types of membrane were used, tubular and hollow fibre, Figures 4.3, 4.4 and 4.5 showing the end of the hollow fibre module.

Figure 4-3 Koch Tubular PVDF Membrane Module

Figure 4-4 End view of Hollow fibre module (PAN)


Figure 4-5 Koch Hollow fibre PAN Membrane Module

Tubular Type

The tubular membranes were made from polyvinylidene fluoride (PVDF) and have a molecular weight cut off (MWCO) of 100 000 daltons. One has a net negative surface charge (Koch Membrane Systems Inc.; HFP-276), the other has a neutrally balanced charge (Koch Membrane Systems Inc.; HFP-278). Both membranes measure 1.52m in length and have an internal diameter of 2.54 cm, with an effective membrane surface area of $0.1m^2$, see Figure 4.6. Both membranes are designed for the filtration of emulsions. The pressure drop across the membrane was typically 0.1 bar which at the highest flow rate of $4m^3h^{-1}$ was around 0.14 bar. A short length of tubing was connected to the permeate outlet of the membrane casing to allow the permeate to be directed to either to the feed tank or to be collected for flux calculation. The permeate outlet can also be completely blocked off for cleaning purposes.

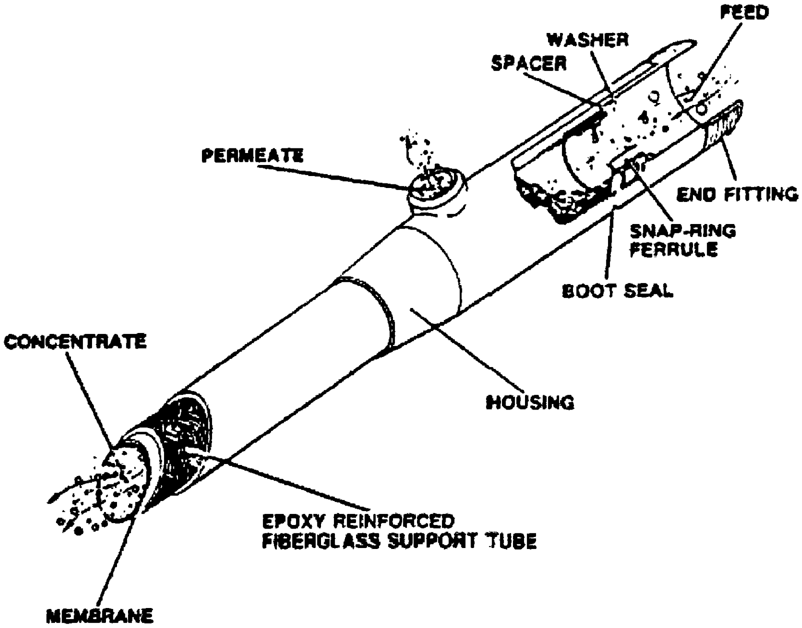


Figure 4-4 Koch PVDF Tubular Membrane Assembly [1]

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[1] Taken from Perry's Chemical Engineering Handbook Volume 7

Hollow Fibre Type

Two different hollow fibre modules were used, one for the separation of oil in water emulsions made from Polyacrylicnitrile 1.143 mm fibre diameter (PAN Koch P/N 0720092 15-45- XM50P) and the other for particle rich effluents, made from Polysulphone 1.1 mm fibre diameter (PS Koch P/N 0720082 14-43-PM50). Both have a module length of 0.64 m and a housing diameter of 0.0762 m with an effective membrane surface area of 1.4 m^2 and a MWCO of 50 000. Both membranes have two permeate outlets that can accommodate various pieces of equipment. Generally the top outlet has a triclover clamp hose tail to allow the connection of a piece of tubing to direct the permeate where required and the bottom outlet accommodates a pressure sensor, enabling an accurate average trans membrane pressure to be calculated in conjunction with the other two pressure sensors.

4.3 *Pilot Plant Operation*

Drain and filling procedure

1. Before the feed tank was filled, ensure that the rig was placed on an even surface and that the feet are locked in position.

❖ At this stage there is no need for the apparatus to be connected to the mains.

2. Check that the feed tank was clean and that the connecting pipe work was free of items that may cause possible blockages.

❖ This can be done by removing the bottom section of pipe from the exit of the feed tank via the triclover clamp.

3. The pipe is then replaced and the clamp tightened, ensuring that the sealing ring is in place to complete the seal. Ensure that valve V1, Figure 4.2 is closed.
4. The starting feed solution is then introduced into the tank via the open top.
5. Valve V1, Figure 4.2 was then opened and the fluid enters the feed pipe to the pump.

6. The priming valve on the pump was then opened and the fluid was allowed to enter the pump until the pump was primed.

To drain the rig, a flexible piece of hose can be connected to the concentrate return pipe.

1. Switch off the rig via the front panel.
2. Carefully remove the membrane module from the rig and replace the pipe blank.
3. The flexible hose was then put to either drain or to a suitable receiving vessel.
4. Valve V3, Figure 4.2 was then slightly opened to allow a low flow and a low pressure was set via the inverter.
5. Switch on the pump and remove the solution from the feed tank.

❖ Be careful not to continue pumping after the level in the tank was such that the pump can be no longer be self primed and air was sucked into the pump.

6. The pump was then stopped.
7. The drain valve on the bottom of the pump was opened and the remaining fluid drained away.
8. Once all the remaining fluid has been emptied, close the pump draining valve.

Setting the Flow and pressure of the system

The required flow and pressure cannot be set automatically from the pump. To ensure that the pressure and flow corresponds to that required for the experiment, the experimental solution can be pumped around the system whilst using the required blank in place of the membrane module. This also allows the temperature of the solution to be stabilised at ~25°C via either heating or cooling using the "cooling" coils in the feed tank. An initial pressure was set on the inverter that corresponds to a slightly greater pressure than that required allowing for some pressure drop that occurs over the flow meter and the pipe work.

The pump was then started via the front panel and the valve V3, Figure 4.2 was then adjusted until the flow meter reading on the front panel was that required for the experiment. Adjustments can also be made to the pressure setting on the inverter so that the average pressure reading on the displays of the panel are those required for the experiment. Once the temperature has stabilised and the operator was happy with the flow and pressure settings, the rig was stopped, the blank then removed and replaced with the required membrane module.

PWF measurement

Before each experiment, the pure water flux of the membrane was measured. Initially the membrane was removed from the rig and the blanking pipe was in place to complete the piping run. Approximately 30l of distilled water was added to the feed tank. The pump was then started and the solution was then brought up to a temperature of ~ 25°C. The flow rate and pressure was then set according to the procedure in Chapter 4.3.2. The permeate flow was sampled over 30 - 60 minutes until an approximately stable value was reached. This value was then used as a benchmark for that particular membrane to compare with the experimental flux.

Rig cleaning

After each experiment the rig was drained and cleaned. This was done to ensure that the experimental solution was removed so that further fouling of the membrane does not occur during the subsequent membrane cleaning.

1. The rig was drained as set out in procedure detailed in Chapter 4.3.1.
2. Valve V1, Figure 4.2 was then placed into the closed position and the used membrane replaced with the appropriate blank.
3. Approximately 50 l of warm water was introduced in to the rig along with 10-20ml of washing-up solution.

4. After the feed tank was filled, a low flow and pressure was used to circulate the cleaning solution for approximately 20 minutes.

- A brush can be used to scrub the inside of the feed tank to remove any deposits that may have built up on the surface of the tank.

6. The rig was then drained and the feed tank was hosed down to remove soap etc whilst the tank was being drained.

- An indication that the rig was clean was when the water exiting from the pump's drain runs clear.

7. Once the rig was clean, the valve V1, Figure 4.2 was shut so as to allow the tank to fill with clean cold water. The pump drain valve was also shut.
8. After approximately 50 l of clean water has been introduced into the tank, the pump was started using the same previous low flow and pressure settings to circulate the clean water. This should remove any remaining soap or possible fouling material that may be left in the pipe work. This was done for approximately 10 minutes.
9. Step 6. was then repeated and the hosing down stopped after approximately 2 minutes so as to allow the system to fully drain.
10. The rig was then left for 15 minutes with the pump drain valve open to ensure that the rig was fully drained.

Permeate Measurement and Sampling

To determine the flux rate of the experiment, the permeate flow was measured using an electronic balance and a stopwatch. The stopwatch was set to the time on the datalogger so that the readings can be matched up with one another. Once the rig was started, it takes approximately 5 seconds for the flow and pressure to be ramped up to values set for that experiment by the inverter on the pump.

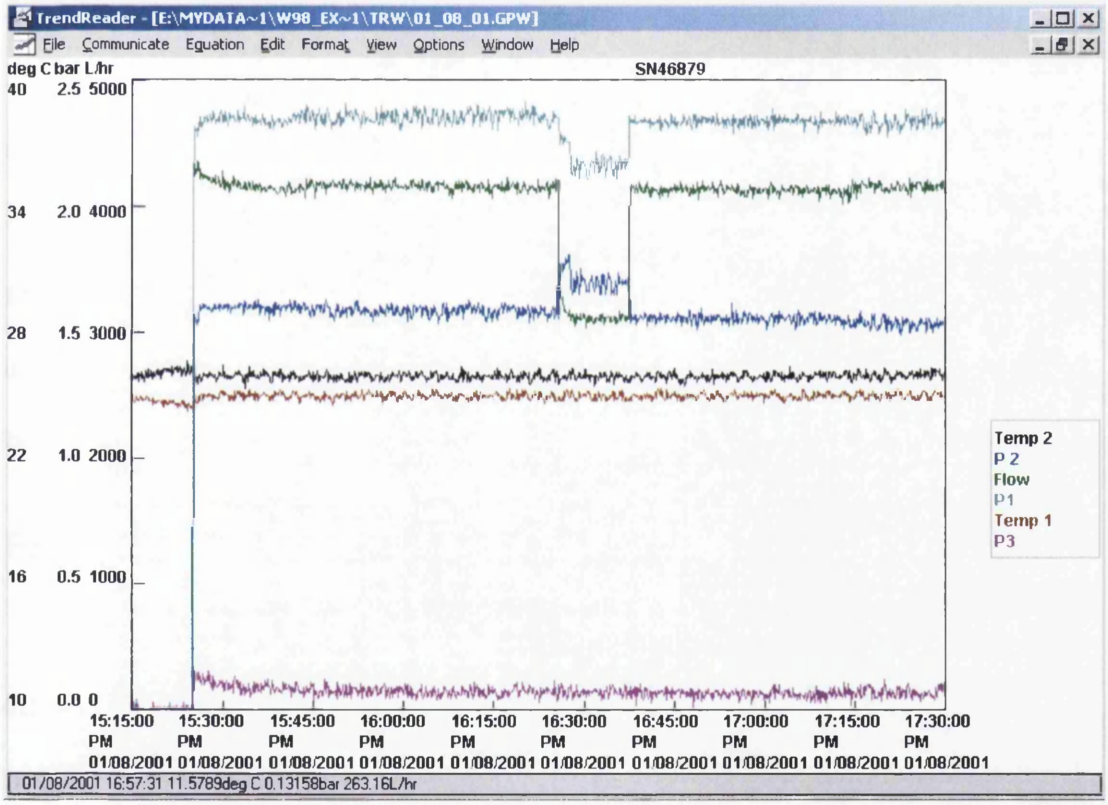
A permeate sample was taken by collecting a sample via the permeate pipe from the membrane over a set period of time, normally ten seconds, in a preweighed beaker. The beaker was then reweighed and the amount collected noted. This was then used to calculate the flux value in L / m^2 h. The beaker was then reweighed and the scales tare, ready for further samples. The sampled permeate was either returned fully to the feed tank or partially retained in a separate sample jar for further analysis with the rest being returned to the feed tank. Due to the size of the membrane surface area, the samples taken were quite large and over a ten second period for the PS membrane, were around 650 g / 10 seconds.

In the majority of experiments, the permeate was returned to the feed tank so that the concentration of the feed solution was kept relatively constant. This concentration will change slightly throughout the experiment due to solute being adsorbed onto the membrane and the possibility of solute passing through the membrane but this was negligible. In a normal experiment the starting volume of sample was 50 l of solution. A composite sample of permeate was collected during the course of the experiment. This was done by collecting approximately 50 ml of permeate, ten times throughout the duration of the experiment. At the end of the experiment, approximately 500 ml of permeate has been collected for analysis in a glass sample jar. This sample was then stored in a refrigerator until the sample was going to be analysed. Typically the sampled was analysed within a 24 hour period.

Datalogger preparation

Before each experiment, the datalogger's memory was cleared and various parameters are set. The number of active channels was determined by what instruments are required to be logged, normally 5 but up to the maximum of 7. The logging rate can be set here and this was checked that the rate was every 8 seconds. Higher log rates can be used but to keep the size of the data file down and not to generate any unnecessary data, 8 seconds was chosen. The datalogger can hold upwards of 27 hours of information using a collection rate of 8 seconds for 5 channels.

On completion of an experiment, the data from the logger was downloaded via the serial port of a computer and stored in the native file format of the ACR Trendreader For Windows Version 1.042 software. This file can then be opened and the data then plotted graphically, see Figure 4.7. Further data analysis can be done by exporting the data file as a comma-separated-variable file for use in spreadsheet programmes, e.g. Excel.



01/08/2001 16:57:31 11.5789deg C 0.13158bar 263.16L/hr

Figure 4-5 Example Datalogger Graph for a Hollow Fibre Run showing Flow , Temperature and Pressures

4.4 Feed Sampling

Cold Mill Emulsion

Once the oil-water emulsion was deemed unfit for its original use in a process, it was removed from the process and sent to be treated or disposal. This was done via pumps, pipes and a system of effluent sumps. To collect a sample of this effluent, it was decided to sample after a titling plate separator that was used to remove large particles that are picked up from the pipe work and other streams that are feed into the water treatment plant.

The effluent was therefore collected after this stage in 25 l jerry cans by sampling from a sample valve placed in pipe work downstream of this unit operation. The valve was initially fully opened to allow any build up of material in the valve to be cleared out so that the sample produced was representative of that in the pipe. After each experiment the jerry cans are cleaned using alkaline cleaners to remove any trace of oil and solids and then rinsed with tap water and then distilled water.

Particle Rich Effluent

The particle rich effluent was sampled from a sample point on a pipe that directs the effluent to a treatment sump. This was a simple ball valve that was normally in the closed position that can be opened to allow the effluent to be sampled. The valve was opened fully and the effluent allowed to flow freely to drain before the sample was collected. This allows any possible build of material in the dead leg of the valve off take to be cleared out and the sample to be representative of the contents of the pipe, i.e. the effluent from the process.

Fresh Emulsion

The Fresh Emulsion was made up from distilled water and a concentrate. The concentrate contains various ingredients of a propriety nature; these are anti-bacterial agents, anti-foams, oil, non-ionic surfactants and stabilizers. The concentrate was supplied from the company Houghton Vaughen.

1. Fill the feed tank with 50 litres of distilled water. This was measured out using a 10-litre graduated nalgene container.
2. Circulate the contents of the feed tank at a low pressure and flow rate to allow the system to reach ~ 25 °C.
3. Weigh out the required amount of concentrate so that the concentration of the Oil-water emulsion was that required for the experiment.
4. Approximately 2 l of distilled water was removed from the feed tank and the concentrate was added to this. This was then mixed in a high vortex mixer for five minutes to ensure good mixing.
5. Add the mixed concentrate and water from step 4 to the feed tank whilst the distilled water was being circulated.

❖ Wash out the weighing beaker with approximately 100ml of distilled water and add the washings to the feed tank.

5. Increase the pressure of the system to ~ 2 bar and the flow to ~ 4 m^3/h and leave to circulate for 30 minutes. This will ensure that the oil-water emulsion was fully mixed.
6. Adjust the flow and pressure to that required during the experiment.
7. Once the system has stabilised, stop the pump.
8. Remove the relevant blank from the system and replace with the required membrane for the experiment.

4.5 Analysis Techniques

All the chemical reagents used in the following analysis procedures were supplied by Fisher Scientific, UK. All analysis was undertaken by the Chemical Services department of Corus Port Talbot except for the sizing experiments. This quality assured full time laboratory service is regularly audited to meet the requirements of certain departments within the works for ISO 14001 and ISO 9001 accreditation. Instruments are regularly calibrated and maintained with traceable standards and procedures for all analysis undertaken within the lab.

Suspended Solids Determination

A sample was filtered through a weighed GF/C filter and the filter was reweighed. The suspended solids concentration was the difference in mass of the filter before and after filtration divided by the volume if sample used.

Reagents

- Double Distilled water should be used throughout
- Acetone
- Petroleum ether (60 – 80°C)

Apparatus

- Filtration apparatus (Whatman)
- GF/C Filter (dried at 105°C) (Whatman)

Analysis Procedure

Place a GF/C filter paper to dry, for at least 2 hrs at 105°C. Weigh the dried filter paper. Wash the dry filter paper with distilled water (100ml) under, shake the sample and filter a measured volume. Remove any remaining solid from the sample container, rinse with water

(100ml) and filter the washings. Rinse the filter with water and, if oily, with acetone and petroleum ether. Dry the filter and residue (105°C) and reweigh.

$$\text{Suspended solids (mg/l)} = \frac{\text{Mass of residue (mg}}{\text{Sample volume (ml)}} \times 1000$$

Solution pH

The temperature-corrected pH was measured with a pH electrode displayed with a meter.

Reagents

- **Distilled water should be used throughout.**
- pH buffer solutions: pH 4, pH 7, pH 8, pH 9.2 and pH 10. These may be prepared from pH tablets or, if available, commercial buffer solutions may be used.

Apparatus

- pH meter and electrode
- ATC probe

Frequency: Each day or shift, before measuring any samples. The calibration was checked with the relevant pH buffer. If the pH reading was +/- 0.1 of the standard, then proceed with the measurement of the samples.

Analysis Procedure

Calibrate using two buffers covering the range expected for the sample. After calibration, check by measuring the pH of another buffer solution. If this pH was within +/- 0.1 of the expected value, proceed with samples measurement, otherwise recalibrate the meter. If any meter will not calibrate, replace the pH electrode. If the meter will still not calibrate, consult the Section Chemist. For detailed calibration consult the relevant pH meter manual. Rinse the electrode with water, place in the sample and allow the reading to become steady. Always rinse the pH electrode between samples

Solution Conductivity

The temperature-corrected conductivity was measured with a conductivity meter and electrode. Conductivity measurements are automatically compensated to 20 °C by the meter. Total dissolved solids are calculated as 2/3 of the conductivity.

Reagents

- Distilled water must be used throughout.
- Potassium chloride (0.01M/0.01N): Dissolve potassium chloride (0.74526g) in water and dilute to 1 litre. If a commercial solution was available, this may be used instead.

Apparatus

- Conductivity meter and electrode.
- Temperature probe (for Unicam meters)

Each day or shift, before measuring any samples. The meter was satisfactory if the reading was within +/- 5% of the standard value i.e.: 1214 - 1342mS cm-1. Proceed with the sample measurements

Analysis Procedure

Potassium chloride (0.01M/0.01N) has a conductivity of 1278mS cm-1 at 20 °C. The calibration of the meter was satisfactory if the reading was within +/- 5% of this i.e.: 1214 - 1342mS cm^{-1}. If the calibration was satisfactory, proceed with sample measurement otherwise check that the correct cell constant has been entered. If not, enter the correct cell constant and repeat the calibration check. If the correct cell constant has been entered, the meter must be calibrated. For detailed calibration, consult the relevant meter manual. For:

- **RADIOMETER CDM210 CONDUCTIVITY METER:** Rinse the electrode with water and place in the sample. Press **SAMPLE** and wait until the reading was steady.
- **UNICAM METERS**: Ensure that the **CAL** and **REF** buttons are released, the **ATC** button was pressed in and the temperature coefficient was set to 2.1. Place the electrode and temperature probe in the sample and wait for the display to become steady.

Total dissolved solids (mg/l) = 2/3 x conductivity

Solution Oil Content

Oil and grease was extracted using a solvent such as tetrachloroethylene or 1,1,2-trichloro-1,2,2-trifluoroethane. The infrared absorbance of the extract was measured at 2930, 2960 and 3030cm^{-1} with an FT-IR spectrometer or at 2960 cm^{-1} with a dispersive ir spectrometer and the concentration of oil in the original sample was calculated.

Reagents

- Sodium chloride
- Sulphuric acid
- Sodium sulphate (anhydrous)
- Tetrachloroethylene or 1,1,2-trichloro-1,2,2-trifluoroethane.

Apparatus

- Separating funnel
- Programmable IR spectrometer and cuvettes

Analysis Procedure

Measure the sample volume and transfer to a separating funnel. Add sodium chloride to produce a concentration of approximately 5% and sulphuric acid (50%) to give a concentration of approximately 0.25%.

Add solvent (25ml) to the bottle, shake and transfer to the separating funnel. Shake the sample, releasing the pressure periodically. Allow the layers to separate and pass the lower layer through a dry, Whatman No 41 filter paper containing sodium sulphate (anhydrous, approx 5 g).

Ensure the sample compartment was clear and the lid open and press **F1**. Place a cuvette containing solvent only and press **F2**. Each sample may be measured by placing a filled cuvette in the sample compartment and pressing **F3**. If the sample volume, solvent volume, dilution factor or cell path length need to be changed from those previously entered, press **F4** and enter the appropriate parameters. To calculate the sample concentration press **F5**.

For further information see FT-IR Instrument Operating Instructions

Place 20mm cuvettes containing unused solvent in both reference and sample compartments and adjust the baseline to approximately 95%. Place a 20mm cuvette containing the sample extract in the sample compartment and scan the spectrum between approximately 2800cm-1 and 3200cm-1.

Calculate the net transmittance of the peak at $2960cm^{-1}$ and read the concentration off the calibration graph.

Results calculation

$$\text{Oil in water (mg/l)} = \frac{\text{mg found x 1000}}{\text{Sample volume (ml)}}$$

Solution Dissolved / Un-dissolved Metals Concentration

Iron, lead, zinc and chromium in aqueous effluents are measured by Atomic Absorption Spectrometry or Inductively Coupled Plasma Optical Emission using an autosampler.

Concentrations of soluble metals are determined by analysis of the sample after filtration. Concentrations of insoluble metals are determined after acid dissolution of the solids retained on the filter. Total metal concentrations are the sum of the soluble and insoluble concentrations.

Reagents

- Hydrochloric acid (S.G.: 1.16 or 1.18)
- Nitric acid (S.G.: 1.42)
- Standard solutions of iron, lead, zinc and chromium (1 000 ppm)

These dilute standard solutions are prepared by adding hydrochloric acid (SG: 1.16 or 1.18, 20ml) to a flask (1000ml), the appropriate volume of the concentrated solutions and dilution with water.

Standard	Volume of Stock (ml)	Equivalent Conc
EPC Blank	0	0
EPC1	0.2ml Pb,Zn,Cr 1.0 ml Fe	0.2ppm Pb,Zn,Cr 1.0 ppm Fe
EPC2	1.0ml Pb,Zn,Cr 5.0ml Fe	1.0 ppm Pb,Zn,Cr 5.0 ppm Fe
EPC3	10.0ml Pb,Zn,Cr 50.0ml Fe	10.0 ppm Pb,Zn,Cr 50.0 ppm Fe

Apparatus

- Measuring cylinders
- Conical flasks
- Filtration apparatus
- Membrane filter
- Perkin Elmer ICP AES Model

Analysis Procedure

- Soluble metals

Mix the sample and filter 100ml of sample through a membrane filter and retain the filtrate.

- Insoluble metals

Transfer the membrane filter and residue to a flask, add nitric acid (S.G/: 1.42, 2ml) and heat until the filter has dissolved. Evaporate to dryness, add hydrochloric acid (S.G.: 1.16 or 1.18, 2ml) and warm gently to dissolve any remaining residue. Add water (30ml) and heat to boiling. Cool and dilute to 100ml.

Aspirate water blank and the standards appropriate for the expected sample concentration. Analyse one of the standards as a sample. If the result was within +/- 5% of the known concentration, aspirate the samples. If the result was not within +/-5% of the known concentration, recalibrate the instrument. If the instrument will not calibrate correctly, consult the Section Chemist. If the sample concentration was outside the calibration range, either dilute the sample to bring it within range or rotate the burner head through 90 degrees.

Analysis can be carried out by an autosampler on the I.C.P. Recall the program "Dailyeff", which will have the analysis tray details. Samples can be added if not routine. For further details, see the Perkin Elmer I.C.P. operating manual.

Particle / Emulsion Sizing

The basic principle employed by the Malvern Mastersizer to determine particle size was low angle laser light scattering (LALLS). When a particle passes through a laser beam, it causes light to be scattered at an angle that was inversely proportional to its size. See Figure 4.8. The laser beam passes through a pinhole at the centre of the detector array. If no particles pass through the beam, all the light falls on to a detector known as an obscuration detector. However, as soon as a particle enters the beam, it scatters light. The Fourier lens collects the light scattered from an ensemble of particles and overlays the common angle of scattering on the detector array. The overlaid data was known as a light energy distribution and there was a direct relationship between this and the particle size distribution that gave rise to it.

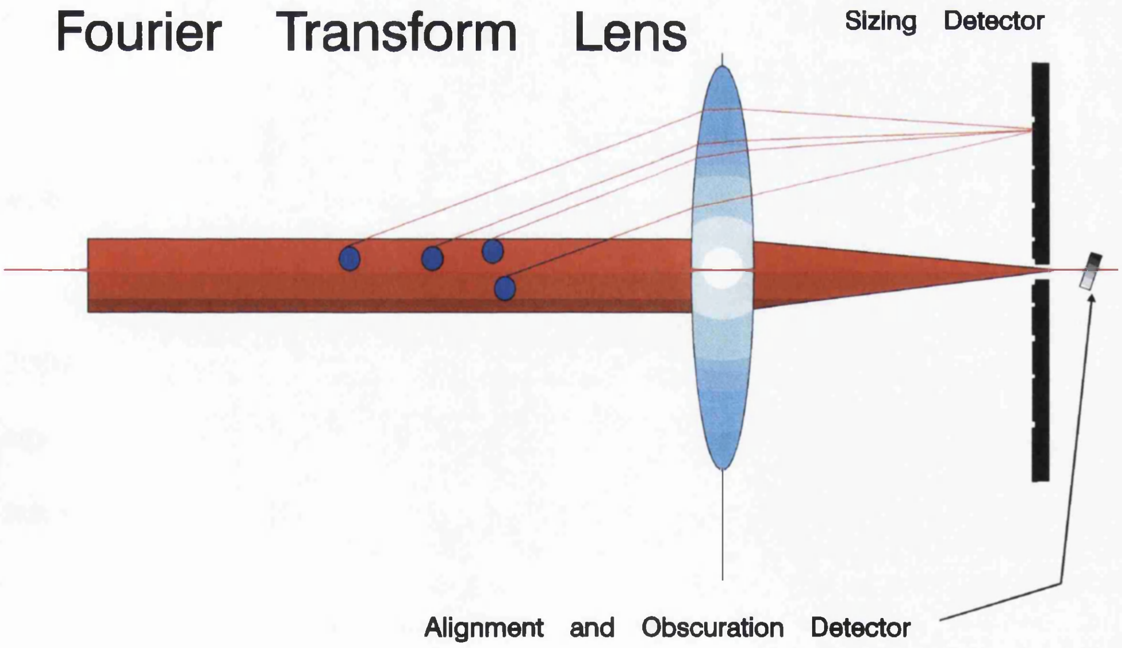


Figure 4-6 Low Angle Laser Light Scattering Principle used by Mastersizer

Reagents

- Double Distilled Water
- Sample Solution

Apparatus

- Malvern Mastersizer Model

Analysis Procedure

The Mastersizer was operated as detailed in the manufactures manual.

Check that the lens present in the unit covers the required diameter range of the sample being sized. The sample presentation unit was filled with distilled water and the circulation pump and stirrer are started at a setting of 5 on the console. The initial background was measured as a baseline to compare with the sample to be measured. The sample to be measured was introduced in the sample presentation unit gradually with the obscurance of the feed being continually monitored. Ideally, the obscurance was around 0.20. A graph and Table was printed out for that particular sample given the number of droplets / particles in a particular droplet diameter range.

4.6 Software and Calculations

The software used to prepare the manuscript was Microsoft Word 2000, Microsoft Excel 2000 was used to calculate the fouling percentage and prepare the graphs. To calculate the amount of fouling after a filtration on the membrane surface, the membrane was bench marked using double distilled water and the membrane resistance $R_{m(0)}$ calculated by:

$$R_{m(0)} = \frac{\Delta P}{\mu J}$$

Where J is the flux measured using the double distilled water. R_m is then calculated throughout the experiment and $R_{m(0)}$ is then taken away from R_m and converted to a percentage:

$$\frac{R_m - R_{m(0)}}{R_m} \times 100$$

5 Filtration of "Waste" Emulsion

5.1 Cold Mill Rolling Emulsion

The purpose of this Chapter was to study the feasibility of using membrane water treatment processes to treat the waste rolling emulsion from a large cold rolling mill. The emulsion is stored in a large tank and then pumped onto the rolls during steel rolling, lubricating the steel surface and cooling the rolls. The emulsion is sampled throughout the day and the biological count measured to determine age and subsequent suitability. If it was determined that the emulsion has aged, a known volume was emptied from the tank and fresh emulsion is then added as make-up.

The emulsion is recycled through the system and the level in the tank maintained, with any other losses, i.e. those caused by leaks etc, being made-up. The emulsion is prepared using deionised water supplied from ion exchange beds and a concentrate containing oil, non-ionic emulsifiers, antioxidants and anti-bacterial agents to stabilise the emulsion. The exact composition is of a proprietary nature and was not made available but like many other emulsions used in cold rolling, the emulsion is of a milky grey appearance, see Figure 5.1. The emulsion is made-up of two parts "concentrate" and 98 parts water, approximately 20 000 PPM of concentrate of which about two thirds is oil.

Figure 5-1 Example of the Typical Emulsion (on left) next to a Permeate Sample

Three membranes were purchased for the filtration of oil-in-water emulsions from Koch, two of a tubular format and the third as a hollow fibre package, furthers details can be found in Chapter 4. The PAN hollow fibre operates at a lower pressure and higher flow rate than the tubular offerings, giving a much larger membrane surface area in a smaller footprint module at a cost of ~£530 per square meter of membrane. Due to difficulties with the cleaning of the PAN membrane and being unable to recover flux, the numbers of experiments using the membrane were limited.

The tubular membranes were made from PVDF; one had a neutral effective membrane surface charge and the other anionic, both at a cost of ~£2500 per square meter. This allowed a general assessment of the different type of membrane materials on the filtration of a waste emulsion stream and of the effect of membrane surface charge

Three basic types of experiment were undertaken:

1. Operation under manufactures recommended conditions,
2. Operation under variable pressure at constant flow
3. Operation under variable flow at constant pressure.

By varying the flow rate passing over the membrane, the effect of shear rate on the membrane fouling surface could be assessed and varying the pressure allowed the assessment of the balance between polarisation effects and membrane resistance.

After each experiment, the membrane was cleaned and benchmarked; details are given in 5.5 Cleaning.

5.2 Sampling and Preparation

All waste emulsion is collected via drains positioned throughout the mill and passed through pipes to a collection sump where it is pumped to a treatment plant, Cold Mill Effluent Plant. As the waste emulsion passes through the pipe and sump system, it becomes mixed with other effluents from the mill and surrounding area. En-route to the treatment plant, several other contaminants are picked up including suspended solids and free oil and it is the mix of effluents that is eventually treated. Due to the varied nature of production, uncontrollable discharges and leaks, the effluent that finally reaches the treatment plant varies from hour to hour. All sampling was taken after a tilting plate separator so that any large suspended solids and floating oil was removed. The samples were taken from a sample valve as detailed in Chapter 4.4 Cold Mill Emulsion and collected in 25 litre jerry cans.

No preparation of the sample was carried out as reproduction of the actual waste emulsion was the aim. The temperature range of the effluent was between 20 and 30°C with steam heating to prevent any free oil build-up during the colder months. Based on this temperature range, the experimental operating temperature of 25°C was deemed appropriate.

5.3 Analysis and Characterisation of Emulsion

After the feed tank has been filled with the sample, the temperature was stabilised by pumping it around the system with no membrane present. A 500ml sample was then removed from the feed tank in a glass sample jar and taken to Port Talbot Works Chemical Labs for analysis of oil, conductivity and pH. This sample will also be used for the sizing experiment, which was undertaken after the filtration run. In some cases, further samples were taken during the experiment for further analysis and sizing.

5.4 Filtration Runs

The manufacturers recommended pressures and flow rates are given below:

Membrane	Pressure / bar	Flow / m^3h^{-1}
Tubular PVDF Neutral	3.5	2
Tubular PVDF Anionic	3.5	2
PAN Hollow Fibre	2	4

Table 5-1 Manufacturers (Koch) Recommended Operating Conditions.

These parameters and a temperature of 25°C, were used as the standard operating conditions for the membranes. Apart from any permeate collected for analysis, all other permeate was returned to the feed tank to maintain a constant feed concentration unless stated otherwise.

5.4.1 Initial Runs to determine basic operation of the process - Tubular

An initial set of experiments were carried out that looked at the general filterability of the emulsion based around the recommended operating conditions. No sizing experiments were carried out for these runs and only the basic analysis was carried out. The data-logger recorded data every eight seconds and the flow and pressure was set as described in Chapter 4 Flow and Pressure Setting, also allowing for temperature stabilisation. Permeate sampling was undertaken as described in Chapter 4 Permeate Measurement and Sampling. During the experimental runs, the permeate was collected therefore increasing the concentration of the oil in the feed tank.

The following table, Table 5.2, summarise the 6 tubular experiments:

	Membrane Type	delta P bar	Actual flow $m^3 h^{-1}$	cross flow velocity $m s^{-1}$	Reynolds Number	Permeability J / P Start	Permeability J / P End	Feed Oil Conc. mg / L	Permeate Oil con mg / L	flux start $L / m^2 h$	flux finish $L / m^2 h$	% drop	% fouling	Volume Permeate collected L	Duration minutes
Run 1	Neutral	3.45	2.945	1.614	44650	30.93	14.21	415	10	106	49.2	54	82	26	300
Run 2	Neutral	3.28	1.871	1.026	27700	33.5	6.6	480	9	113	22	81	91	20	300
Run 3	Neutral	3.36	1.901	1.043	29000	35.8	10.58	380	13	120	36	70	87	20.9	300
Run 4	Anionic	3.41	3.460	1.898	52400	25.65	15.12	401	11	87	51	42	79	44.5	475
Run 5	Anionic	3.27	1.802	0.99	26700	22.29	8.62	388	10	75	29	61	89	17	328
Run 6	Anionic	3.31	1.893	1.04	29100	30.45	11.48	335	7	101	38	62	86	21.4	300

Table 5-2 Initial Filtration Runs using Tubular Membranes – Permeate collected

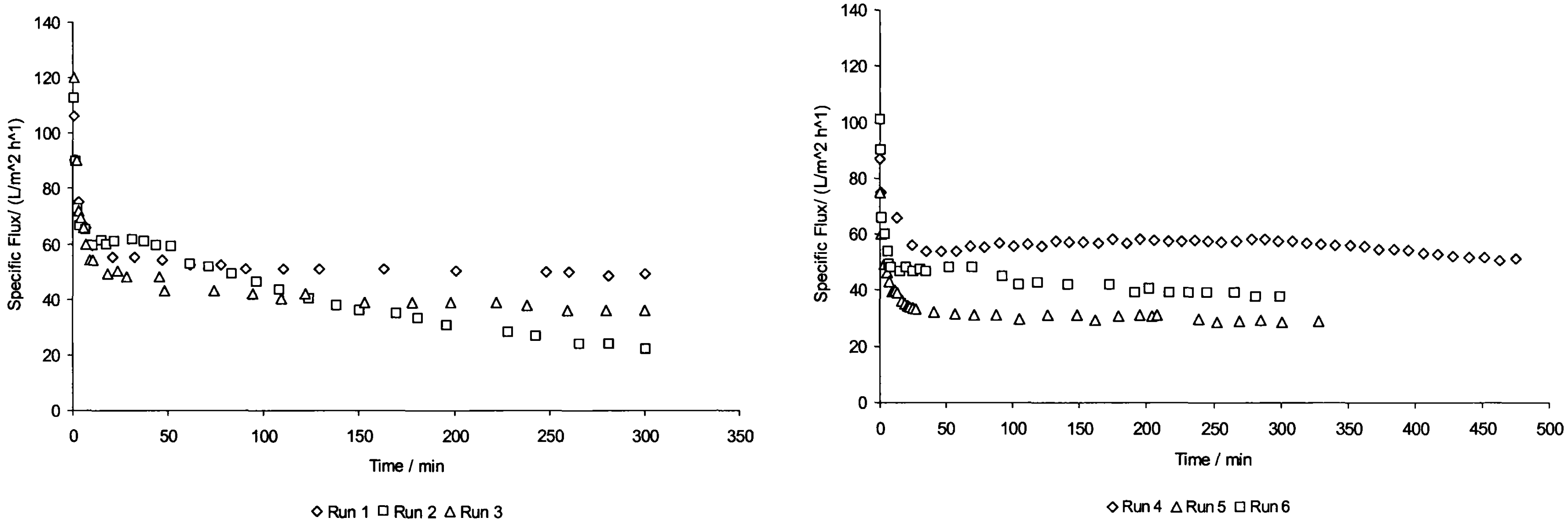


Figure 5-2 Flux graphs for Tubular Runs 1-3 (Neutral Membrane) and Runs 4-6 (Anionic Membrane)

No sizing experiments were carried out for these initial runs and the flow rate was varied for runs 1 and 4 to over 50% of the recommended flow rate. At these higher flow rates, the final flux values were the highest for each membrane and the percentage of membrane resistance due to fouling was the lowest. This is expected behaviour as the shear rate is proportional to cross flow velocity was at its highest. During these experimental runs, the permeate was collected so that the feed concentration was increasing with time. Except for Run 2 (Neutral), there was very little change in the flux with time even though the concentration was increasing. For Run 2, the starting oil concentration was the highest and the final concentration in the feed would also have been the highest.

For all of the experiments, permeate quality was excellent. The operation at higher flow rates and therefore higher specific fluxes will need to be traded off with energy considerations and membrane area as pressure drop will be increased across the membrane tube at the higher velocities. All the experiments were carried out well in the turbulent region of flow.

5.4.2 Tubular PVDF Neutral Membrane

Normal Conditions

Two experiments were carried out under normal operating conditions using the neutral membrane. These experiments looked at the typical fluxes expected when operating under "normal" conditions giving an overall indication of the filterability of the waste but included more detailed analysis of both the feed and permeate than Runs 1-3. These are comparable to flux values given in literature for similar membranes, 50 L m^{-2} h^{-1} from [24] based on a "real" system, between 30 and 50 L m^{-2} h^{-1} from [92] based on ship-waste emulsions and 30-50 L m^{-2} h^{-1} based on a prepared emulsion taken from [108]. The actual operating conditions are presented in Table 5.3:

Run	Delta P bar	Flow m^{3}h^{-1}	Oil Conc. (Start) PPM	Oil Conc. (End) PPM	K μScm^{-1}	pH	Flow m^{3}h^{-1}
7	3.53	2.05	505	316	276	5.7	2.05
8	3.54	2.00	615	217	290	6.1	2.00

Table 5-3 Actual Operating conditions for "Normal" Filtration using PVDF Neutral Membrane.

The two experimental runs were conducted for 100 minutes, which allowed steady state to be reached fully. Figure 5.3 shows the flux curves for Run 7 and Run 8:

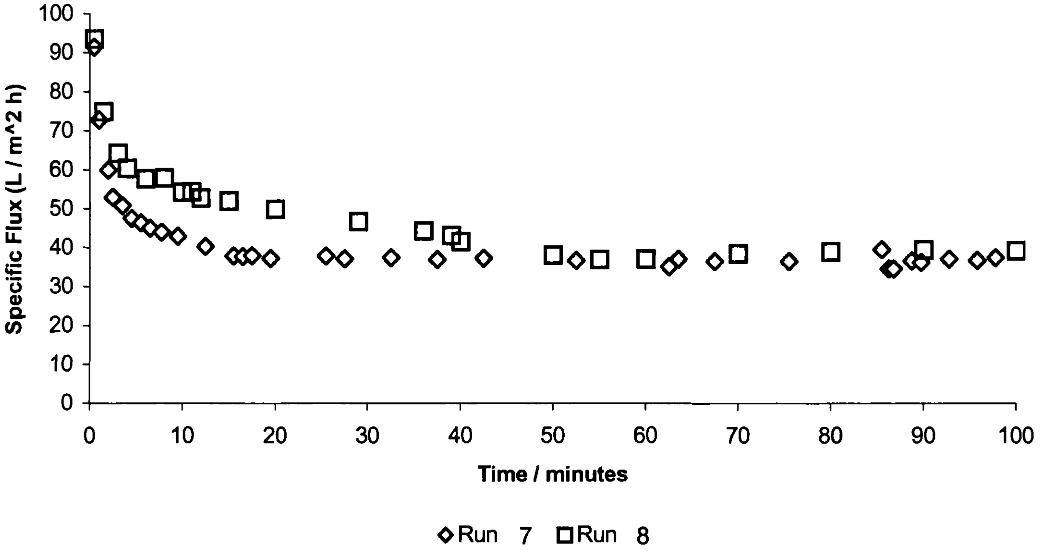


Figure 5-3 Flux Decline during the filtration of "real" emulsion using Tubular PVDF Neutral Membrane under Normal conditions Runs 7 and 8.

As is typical for cross flow membrane filtration experiments under constant operating conditions, the initial high flux value drops rapidly with time. As the filtration progressed, a flux decline from the initial value of ~91 L m^{-2} h^{-1} to ~ 38 L m^{-2} h^{-1} was observed after 15 minutes for Run 7, a drop of 58%, and an initial value of ~94 L m^{-2} h^{-1} reduced to ~ 37 L m^{-2} h^{-1} after 50 minutes for Run 8, a drop of 61%. The flux decline was attributed to the initial formation of the concentration polarisation layer at the membrane surface and membrane fouling, [65]. There was a slight further drop in flux for Run 7 to ~36 L m^{-2} h^{-1} whilst Run 8 saw a slight increase in flux to ~ 40 L m^{-2} h^{-1}.

The composite sample of permeate had a measured oil concentration of 4 PPM for Run 7, resulting in over 99% removal of oil and a value of 12 PPM for Run 8, resulting in 97% oil removal when based on average feed oil concentrations. ICP AES was also undertaken on the permeate sample with an iron concentration of 0.3 PPM and <0.1 PPM for zinc, lead and chromium.

The fouling graph, Figure 5.4, plots the percentage due to fouling of the membrane with time. This was the difference between the total membrane resistance during the experiment and the clean membrane resistance calculated before the experiment. The final values of 77 % of total membrane resistance caused by fouling are the same for each run.

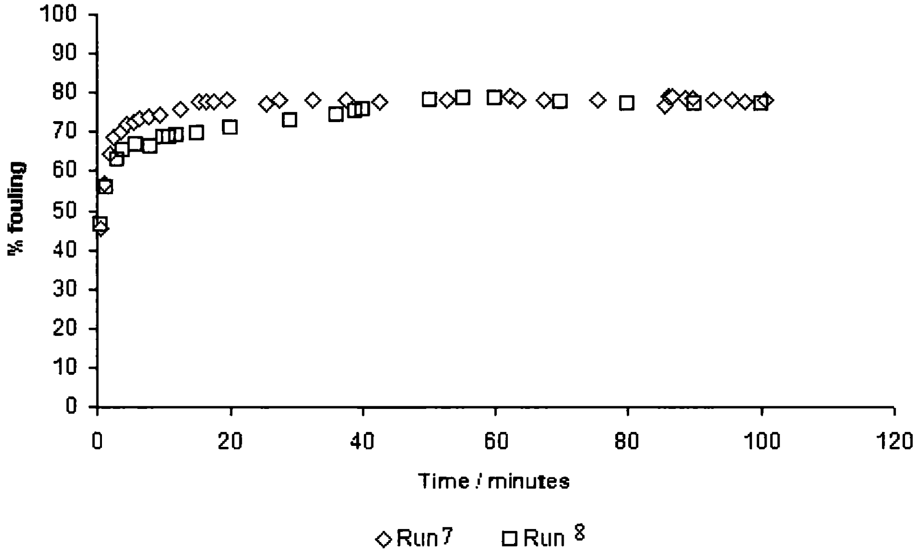


Figure 5-4 Percentage of Total membrane resistance due to fouling of the Neutral Membrane – Normal Conditions Run 7 and Run 8.

Figure 5.5 shows the droplet size distribution for Run 7 – Start and End:

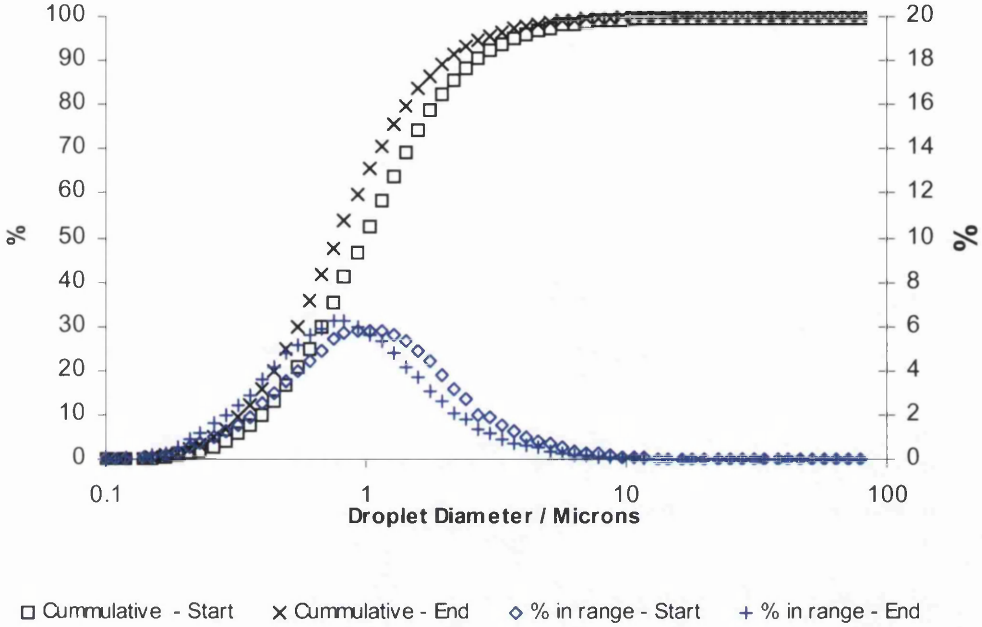


Figure 5-5 Percentage by Volume of Emulsion Droplet Size Distribution for Run Seven – Start and End

The change in droplet size from start to the end was very small, with the average droplet size actually becoming smaller by the end of the filtration. Figure 5.6 shows Run 8:

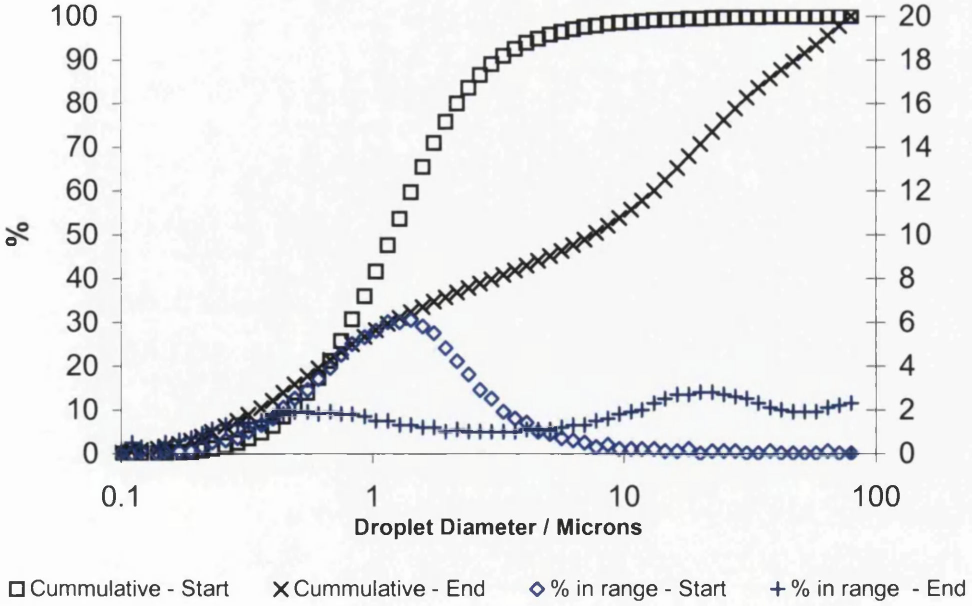


Figure 5-6 Percentage by Volume of Emulsion Droplet Size Distribution for Run 8 – Start and End

The slight increase in flux observed during Run 8 could possibly be attributed to the larger droplet size producing a looser fouling layer. During both Run 7 and Run 8, a slight foaming was observed and free oil was captured in the foam. Although there was only slightly more foaming in the case of Run 7, free oil was also observed sticking to the sides of the vessel. This was supported by the fact that there was a noticeable drop in oil concentration in the feed between the start and end of each experiment, suggesting that the emulsion was becoming unstable.

In the case of Run 7, the decrease in stability was noticeably less as supported by the smaller change in concentration when compared to Run 8 and similar droplet diameter between the start and end. Due to the unstable nature of the emulsion, the increased oil concentration of Run 8 permeate was partially attributed to the emulsion possibly being deformed and "pushed" through the membrane. The percentage of droplets in the narrower range of 0.1 to 0.3 microns had also increased during Run 8.

Variable Pressure (Constant Flow)

Three experiments, Runs 9-11, were carried out under variable pressure at constant flow, see Table 5-4. These experiments looked at the effect of transmembrane pressure on the filtration of "waste" emulsion.

Run	Oil Conc. (Start) PPM	Oil Conc. (End) PPM	K μScm^{-1}	pH	Pressure bar	Flow m^3h^{-1}
9	91	83	278	6.1	3 – 4.4	1.94
10	580	572	300	5.9	2.9 – 4.4	2.03
11	196	180	251	6.1	1.02 – 3.03	2.05

Table 5-4 Operating conditions for Variable Pressure Filtration using PVDF Neutral Membrane.

The initial flow and pressure settings were set as described in Chapter 4.3.2 Flow and Pressure Setting. The pressure and flow rate were controlled by adjusting V3 and using the inverter on the pump's motor. This method was used to change the pressure almost instantaneously for Run's 10 and 11 whereas for Run 9, the pump was stopped and the inverter pressure altered and V3 adjusted whilst no fluid was pumped.

Run Nine

The effect of the "stop–start" approach can be seen on the flux graph, Figure 5.7. There was a drop of 62% from the initial flux value, 90 L m^{-2} h^{-1} to the steady state value of 34 L m^{-2} h^{-1} with smaller drops from the new initial flux values recorded after each change in pressure to the subsequent steady state values. The Table 5-5 summarises Figure 5.7. The gel polarisation model predicts that an increase in pressure produces a temporary increase in flux which results in more solute to the gel layer and a subsequent increase in thickness of the gel layer thereby reducing the flux to the original level. This was evident in the results for this experiment as although the pressure was increased, the original steady state flux was eventually reached.

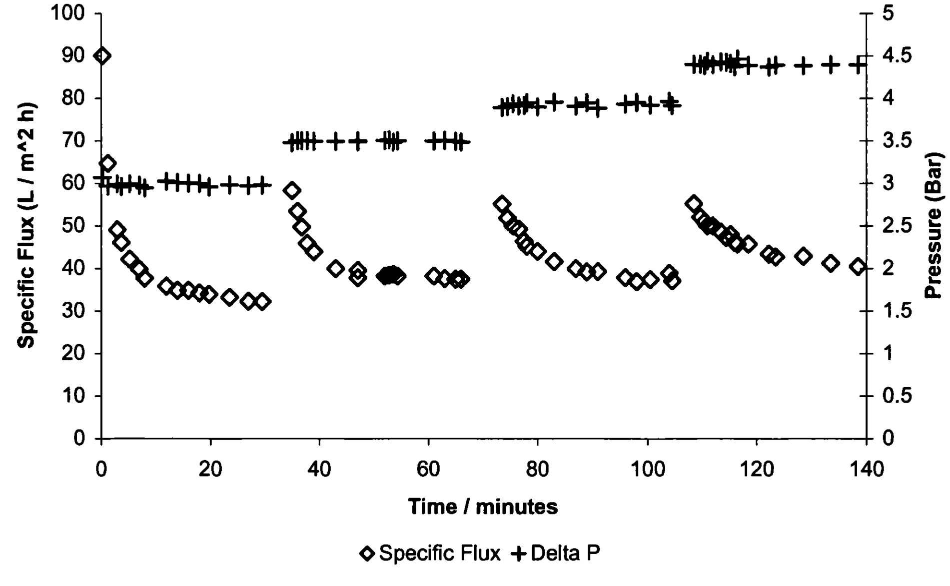


Figure 5-7 Variation in Specific Flux during the filtration of "real" emulsion using Tubular PVDF Neutral Membrane under Variable Pressure conditions – Run 9.

Pressure Settings	Average P bar	J initial L m^{-2} h^{-1}	J steady state L m^{-2} h^{-1}	J final L m^{-2} h^{-1}	Time to steady state minutes
P1	3.00	90	34	32	14
P2	3.50	58	38	37	16
P3	3.92	55	39	37	18
P4	4.40	55	41	40	22

Table 5-5 Summary of Flux values observed during the filtration of "real" emulsion using Tubular PVDF Neutral Membrane under Variable Pressure conditions – Run 9 "Stop –Start" conditions.

Very little foaming or free oil was seen during the experiment and the droplet size distribution was consistent from start to end, see Figure 5.8, suggesting that the emulsion was stable.

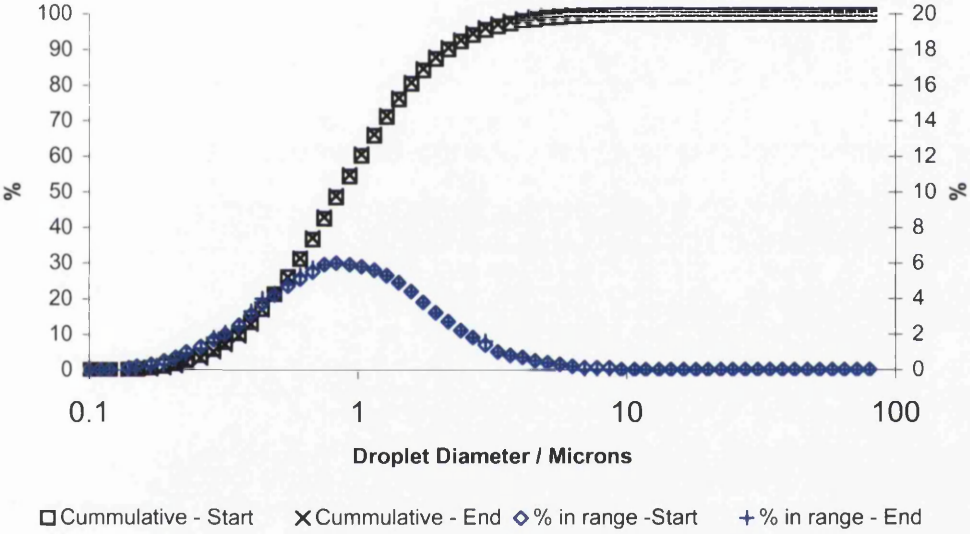


Figure 5-8 Percentage by Volume of Emulsion Droplet Size Distribution for Run 9 Variable Pressure – Start and End

The concentration of oil in the permeate was 10 PPM via a composite sample taken during the two lower pressure settings, resulting in an oil rejection of 89%. The composite sample taken during the two higher pressures produced a permeate with an oil concentration of 9PPM, and oil rejection of ~90%. These are significantly lower values for the rejection of oil compared to other experiments but still result in a high quality permeate. Although the permeate also contained an average of 2 PPM of insoluble iron which was higher than normal, there appeared to be no obvious effect on the flux rates during the experiment.

Run Ten

The pressure and flow adjustment was made instantaneously during Run 10. All changes were made during filtration, with no time spent with the flow stopped. Figure 5-9 shows the transient operation of the run:

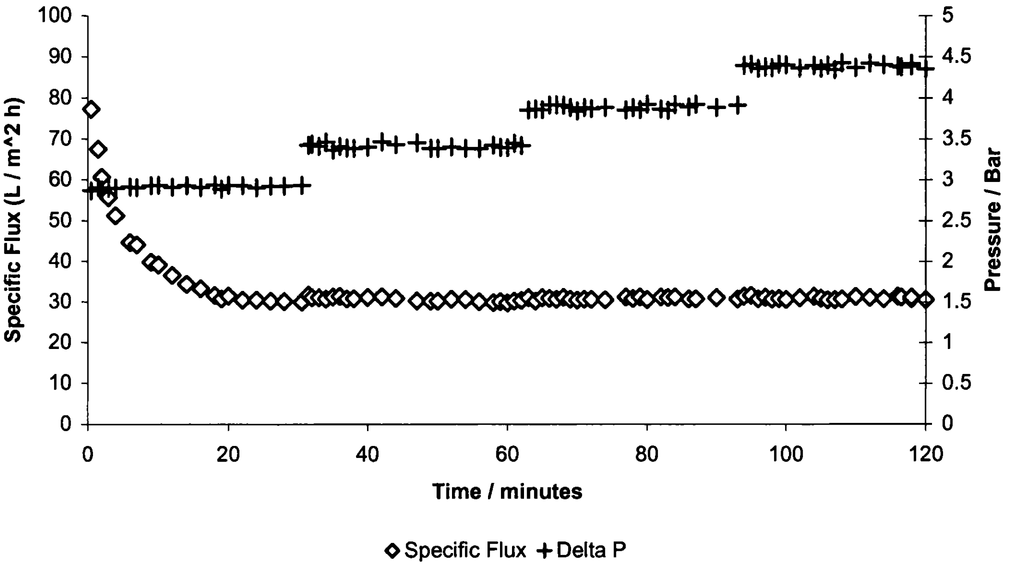


Figure 5-9 Variation in Specific Flux during the filtration of "real" emulsion using Tubular PVDF Neutral Membrane under Variable Pressure conditions – Run 10.

The initial flux during Run 10 of ~ 77 L m^{-2} h^{-1}, although high, was less than previous experiments using the membrane. After 22 minutes the steady state was reached, producing a flux of 30 L m^{-2} h^{-1}, again slightly lower than expected, a drop of 61% from the initial flux. As the pressure was increased, a very small increase in flux was seen which with time falls to the original steady state value of 30 L m^{-2} h^{-1}. This was the same for two further increases in pressure, with a flux value of ~ 30 L m^{-2} h^{-1} being recorded at an average transmembrane pressure of 4.39 bar, showing characteristics of gel polarisation.

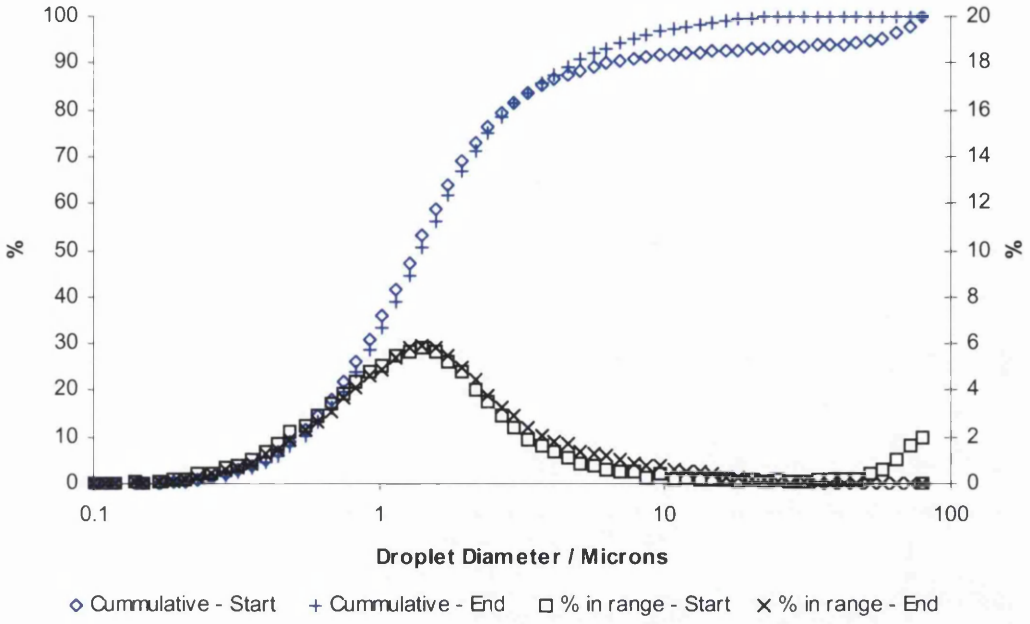


Figure 5-10 Percentage by Volume of Emulsion Droplet Size Distribution for Run 10 Variable Pressure – Start and End

During Run 10 only slight foaming was seen during the experiment and there was little variation in the droplet size distribution between the start and end, see Figure 5-10. The oil concentration analysis also only varies slightly, suggesting that the emulsion was stable throughout the experiment. A composite sample was taken for the two lower pressures and another covering the two higher pressures, both resulted in a permeate oil concentration of 12 PPM, a rejection of ~ 98%.

Run Eleven

Again during this run, the pressure and flow adjustment was made immediately whilst the system was running. The experiment used a lower pressure operating range, with a starting pressure of ~ 1 bar and increased in 0.5 bar steps to 2 bar and a final increase in pressure of 1 bar to take the end operating pressure to 3 bar, approaching that used in normal conditions.

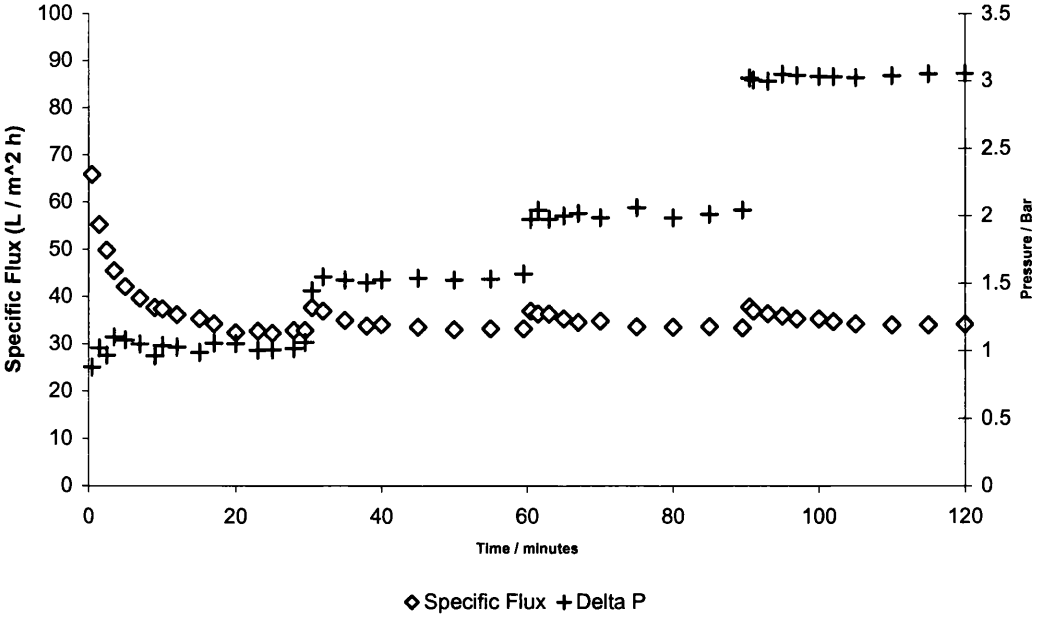


Figure 5-11 Variation in Specific Flux during the filtration of "real" emulsion using Tubular PVDF Neutral Membrane under Variable Pressure conditions – Run 11.

The lower initial starting flux of ~66 L m^{-2} h^{-1} was expected due to the lower transmembrane pressure of 1.02 bar, with a steady state flux of 32 L m^{-2} h^{-1} reached after 23 minutes. An increase in the time taken to reach steady state was expected, as the pressure force driving the feed towards the membrane was less, therefore the rate of fouling should be less. During Run 11 the increase in pressure brings about a more marked increase in temporary flux that decreases with time back towards the steady state flux originally achieved at the initial lower pressure setting.

At the final pressure of 3.03 bar, the steady state flux has only increased to 34 L m^{-2} h^{-1} from an initial steady state flux of 32 L m^{-2} h^{-1} at 1 bar, despite a tripling in pressure. Despite the lower concentration of oil in the bulk, the final steady state flux obtained at 3.03 bar was similar to previous experiments. The droplet sizing experiment produced results very similar to Figure 5-10, confirming the stability of the emulsion throughout the experimental run. The lower pressure composite permeate sample contained 10 PPM oil and 0.5 PPM of soluble iron and the higher pressure sample contained 8 PPM oil and 0.2 PPM of iron, with a membrane oil rejection of 95% and 96% respectively.

Variable Flow (Constant Pressure)

Three experiments were carried out under variable flow with constant pressure, see Table 5-6. These experiments were used to look at the effect of the flow rate and therefore hydrodynamic conditions on the filtration of "waste" emulsion.

Run	Oil Conc.. (Start) PPM	Oil Conc.. (End) PPM	K μScm^{-1}	pH	Pressure bar	Flow m^3h^{-1}
12	401	227	269	6.1	3.30	1.43-2.96
13	388	302	309	5.6	3.37	1.45-3.10
14	1090	966	319	6.1	3.48	1.52-3.13

Table 5-6 Operating conditions for Variable Flow Filtration using PVDF Neutral Membrane.

The flow and pressure were adjusted whilst the system was running and the step change was affected almost instantly. Each experiment was undertaken using the highest flow rate as the starting point. This was used to minimise initial fouling with more fouling naturally expected at lower flows. The flow was decreased in a step-wise fashion by approximately 0.5 m^3h^{-1} each time, decreasing the amount of shear over the membrane surface.

Run Twelve

A starting flow rate of ~ 3 m^3 h^{-1} was used which was still well within the pump's ability to maintain the pressure, with a final flow rate of 1.5 m^3 h^{-1}. The following table, Table 5.7, summarises the flux graph presented in Figure 5.12.

Flow rate	Average Flow m^3h^{-1}	J initial $L\ m^{-2}\ h^{-1}$	J steady state $L\ m^{-2}\ h^{-1}$	J final $L\ m^{-2}\ h^{-1}$	Time to steady state minutes
F1	2.96	116	48	47	16
F2	2.39	44	36	36	11
F3	1.86	35	26	26	18
F4	1.43	26	19	19	24

Table 5-7 Summary of Flux values observed during the filtration of "real" emulsion using Tubular PVDF Neutral Membrane under Variable Flow conditions – Run 12.

The value of 116 L m^{-2} h^{-1} was significantly higher than previous experiments using a waste emulsion. Steady state was reached after 16 minutes, giving a value of 48 L m^{-2} h^{-1} a drop in flux of ~ 60%. With decreases in flow rate corresponding to decreases in the flux. The rate of flux decline also decreases with decreasing flow rate. At a flow rate comparable to other experiments, F3, the steady state flux value of 26 L m^{-2} h^{-1}, was less than expected, suggesting that the membrane has fouled more over the duration of the experiment.

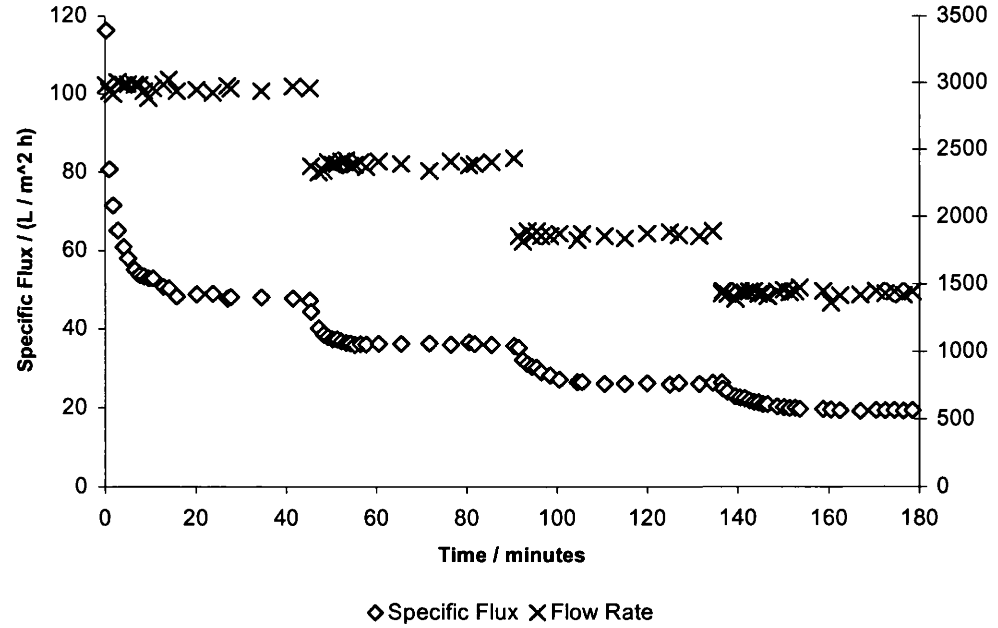


Figure 5-12 Variation in Specific Flux during the filtration of "real" emulsion using Tubular PVDF Neutral Membrane under Variable Flow conditions – Run 12.

Figure 5.13 shows the amount of membrane fouling based on the pure water flux before the experiment at ~3.5 bar and ~2 m^3 h^{-1}, also plotted on the graph was a normal fouling plot based on Run 8.

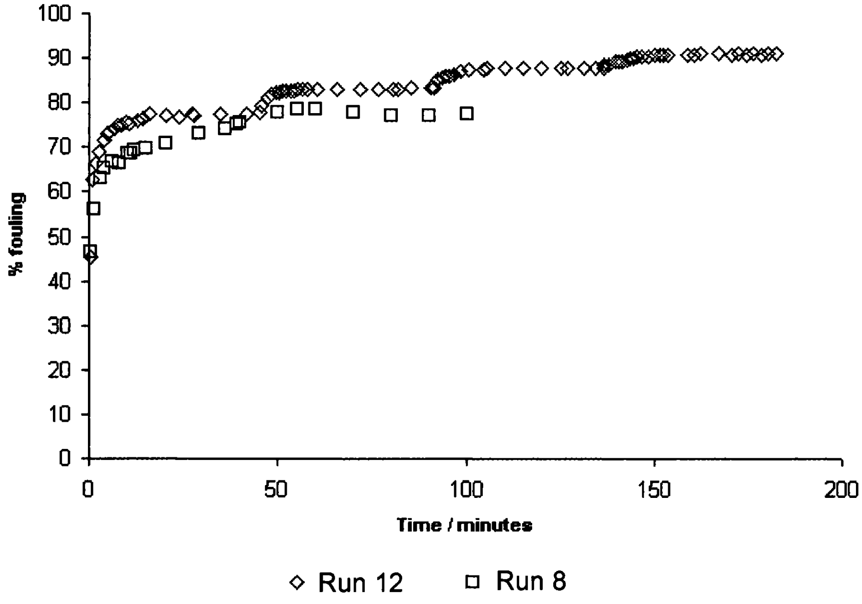


Figure 5-13 Percentage of Total membrane resistance due to fouling of the Neutral Membrane Run 12 –Variable Flow, and Run 8.

As the flow rate was reduced, the percentage fouling increases as the shear effect of the feed over the membrane surface was reduced. This can be clearly seen in Figure 5.13 with the rate of fouling also affected by the reduction in flow. In the case of the Run 8, a general increase in fouling was observed throughout the experiment and remains constant at steady state.

A large amount of foaming was seen at the start of the experiment due to the high flow rate used, with foaming occurring throughout. Free oil was seen on top of the foam and sticking to the sides of the feed tank. The permeate oil concentration was measured as 29 PPM, oil rejection of 92%, with soluble iron concentration of 2.5

PPM. This higher oil concentration suggesting that free oil had been able to enter the membrane pores and been forced through the membrane and into the permeate.

Run Thirteen

As in Run 12, the initial starting flow rate was ~ 3 $m^3\ h^{-1}$, with step decreases of 0.5 $m^3\ h^{-1}$ to a final flow rate of ~ 1.5 $m^3\ h^{-1}$. The Flux graph is presented in Figure 5.14 and summarised in Table 5.8.

As expected, the initial flux of ~87 L $m^{-2}\ h^{-1}$ declines, reaching a steady state value of 46 L $m^{-2}\ h^{-1}$ after 12 minutes, a drop of 47%. Each further decrease in flow results in a further decline in flux. As the flow was adjusted, the rate at which the flux drops becomes less after the initial rapid drop during flow one. This was seen in the time taken to reach steady state after each adjustment in flow, following a similar pattern to Run 12.

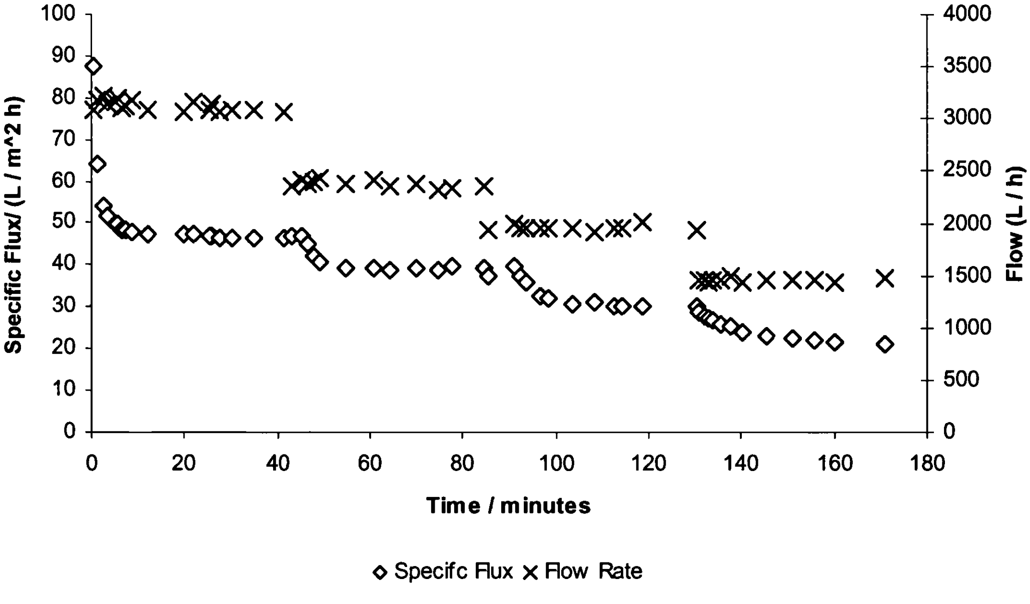


Figure 5-14 Variation in Specific Flux during the filtration of "real" emulsion using Tubular PVDF Neutral Membrane under Variable Flow conditions – Run 13.

Flow rate	Average Flow m^3h^{-1}	J initial $L\ m^{-2}\ h^{-1}$	J steady state $L\ m^{-2}\ h^{-1}$	J final $L\ m^{-2}\ h^{-1}$	**Time to steady state minutes**
F1	3.10	87	47	46	12
F2	2.37	46	39	39	9
F3	1.95	37	31	30	19
F4	1.45	29	21	21	30

Table 5-8 Summary of Flux values observed during the filtration of "real" emulsion using Tubular PVDF Neutral Membrane under Variable Flow conditions – Run 13.

The droplet sizing experiments showed an unusually high percentage of smaller droplets, with more than 50% of the droplets being less than 0.74 micron in diameter. Figure 5.15 shows the change in droplet size from start to end of the experiment. The permeate contained 13 PPM oil and 10.8 PPM of iron. The smaller droplet diameter suggests that a tighter packed fouling layer was formed and results in the reduced flux values seen throughout the experiment. The unusually high amount of iron in the permeate could also be a cause of fouling.

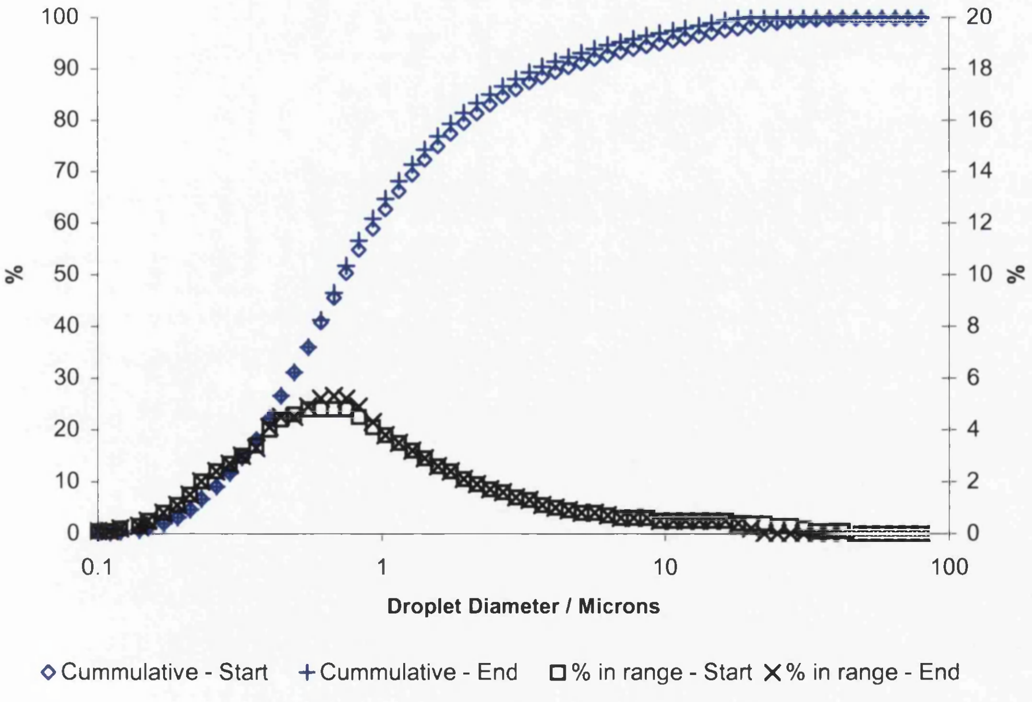


Figure 5-15 Percentage by Volume of Emulsion Droplet Size Distribution for Run 13 Variable Flow – Start and End.

Run Fourteen

As in the previous variable flow experiments, Run 14 used a starting flow rate of 3 $m^3 h^{-1}$, with 0.5 $m^3 h^{-1}$ step changes to a final flow rate of 1.5 m3 h^{-1}. The flux graph is presented in Figure 5.16 and summarised in Table 5.9. An initial flux of 107 L $m^{-2} h^{-1}$ was measured with a steady state value of 59 L $m^{-2} h^{-1}$ being reached after 8 minutes, corresponding to a drop in flux of 45%. This more rapid drop in flux expected due to the high oil concentration in the feed and the stability in the emulsion remaining throughout the experiment.

Each subsequent reduction in flow rate corresponding to a drop in flux of about 10 L $m^{-2} h^{-1}$ from the new initial flux. The time taken to reach steady state also increases with each drop in flow rate as was observed in previous experiments.

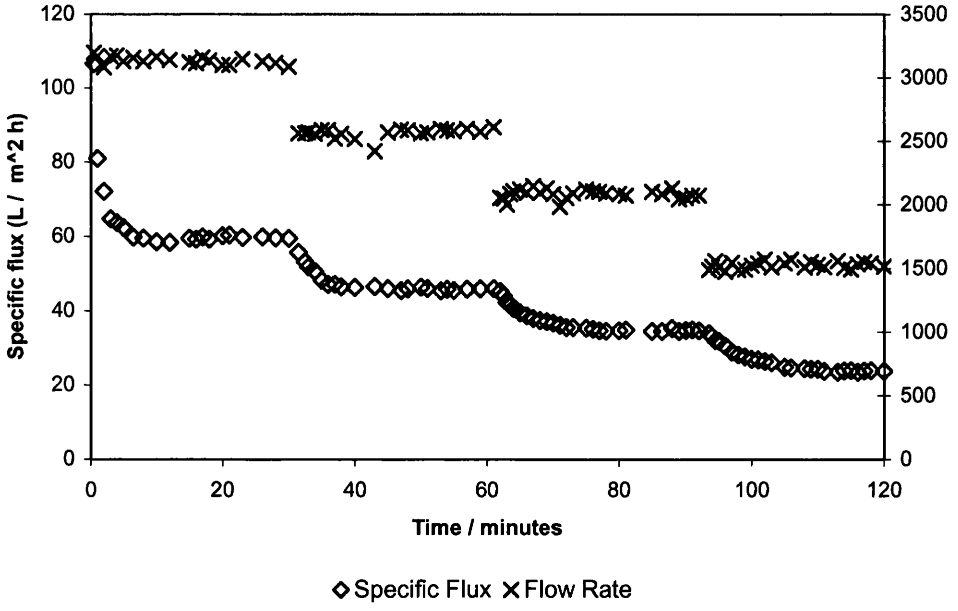


Figure 5-16 Variation in Specific Flux during the filtration of "real" emulsion using Tubular PVDF Neutral Membrane under Variable Flow conditions – Run 14.

Flow rate	Average Flow m^{3}h^{-1}	J initial L m^{-2} h^{-1}	J steady state L m^{-2} h^{-1}	J final L m^{-2} h^{-1}	Time to steady state minutes
F1	3.13	107	59	59	8
F2	2.56	55	46	45	9
F3	2.08	45	35	34	11
F4	1.52	34	24	23	19

Table 5-9 Summary of Flux values observed during the filtration of "real" emulsion using Tubular PVDF Neutral Membrane under Variable Flow conditions – Run 14.

A composite permeate sample taken over the four flow changes had an oil concentration of 9 PPM, resulting in a membrane rejection value of 99% and iron content of 1.4 PPM. The oil droplet diameter varied negligibly over the duration of the experiment, see Figure 5.17, with a slight overall reduction in diameter from start to end. At a flow corresponding to normal conditions, a steady state flux value of 35 L m^{-2} h^{-1} was lower than those recorded under experiments conducted under normal conditions but higher than the previous variable flow experiments, Run 12 and Run 13, despite a higher concentration of oil in the feed.

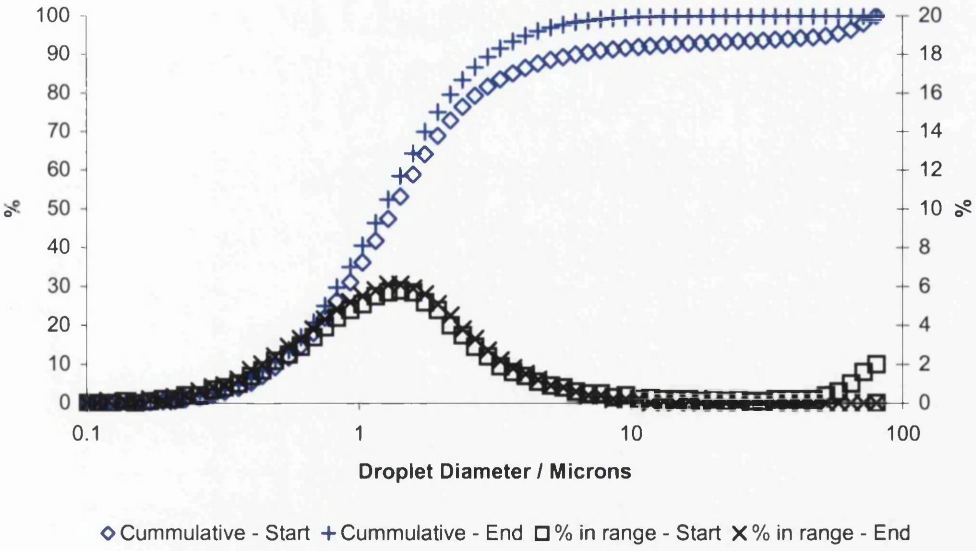


Figure 5-17 Percentage by Volume of Emulsion Droplet Size Distribution for Run 14 Variable Flow – Start and End.

Looking at Figure 5.18, marked increases occur in fouling corresponding to changes to flow rate, suggesting that fouling was a function of flow rate.

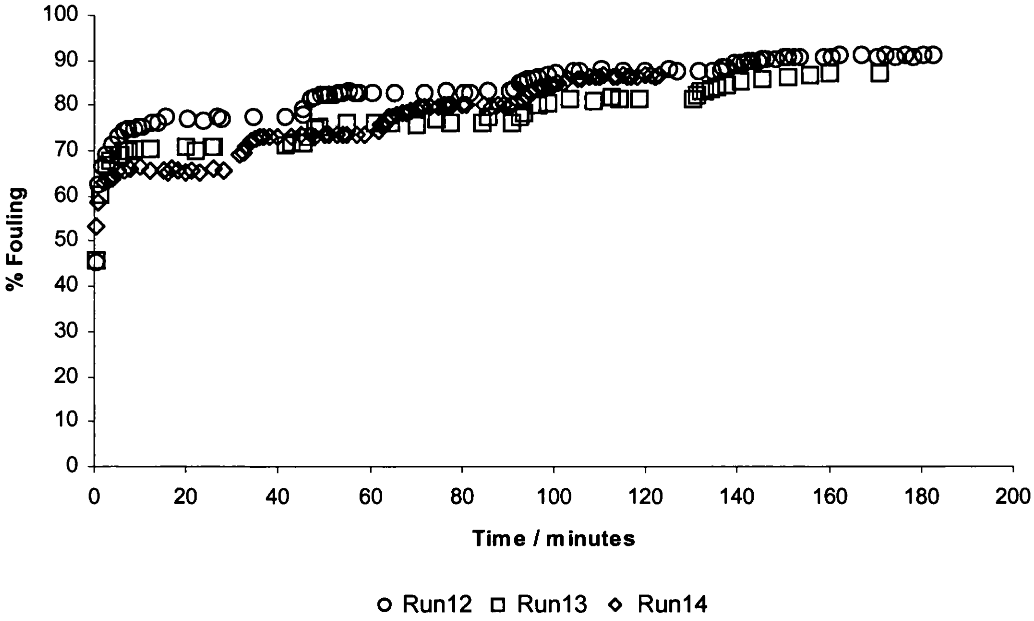


Figure 5-18 Percentage of Total membrane resistance due to fouling - Variable flow conditions – Neutral Membrane- Runs 12 to 14.

5.4.3 Tubular PVDF Anionic Membrane

Normal Conditions

Two experiments were carried out under the manufacturers recommended operating conditions as detailed in Table 5.1 The actual conditions used in the experiments are given in Table 5.10. These experiments allow us to compare fluxes given by [24] and [92] as well as looking at the potential effect of surface charge on filtration by comparing them with the results from Tubular Neutral. The operating conditions are similar to those carried out using the neutral membrane with differences occurring in the feed oil concentration, with the experiments being conducted over 100 minutes.

Run	Oil Conc. (Start) PPM	Oil Conc. (End) PPM	K μScm^{-1}	pH	Pressure bar	Flow m^3h^{-1}
15	650	505	270	5.7	3.49	2.04
16	99	85	345	6.6	3.49	2.00

Table 5-10 Actual Operating conditions for "Normal" Filtration using PVDF Anionic Membrane Runs 15 and 16.

In Run 15, the initial flux of ~ 101 L m^{-2} h^{-1} drops to its steady state value of ~ 40 L m^{-2} h^{-1} after 21 minutes, a drop of 60%. After 100 minutes of Run 15, the flux value has risen slightly to 41 L m^{-2} h^{-1}. A higher initial flux of ~ 129 L m^{-2} h^{-1} was measured during Run 16 with a steady state value of ~ 50 L m^{-2} h^{-1} being obtained after 19 minutes, a drop of 69%. After 100 minutes of Run 16 the flux has dropped slightly to 49 L m^{-2} h^{-1}. The higher initial and final flux values of Run 16 are expected due to the lower oil concentration in the feed. The percentage drop in flux in both experiments was similar to values recorded for the Neutral membrane under normal conditions, 58% and 61% respectively. Permeate for Run 15 contained 2 PPM of oil, a rejection of >99% and for Run 16, 5 PPM of oil and a rejection of 91%. Figure 5.19 shows the flux graph for Runs 15 and 16.

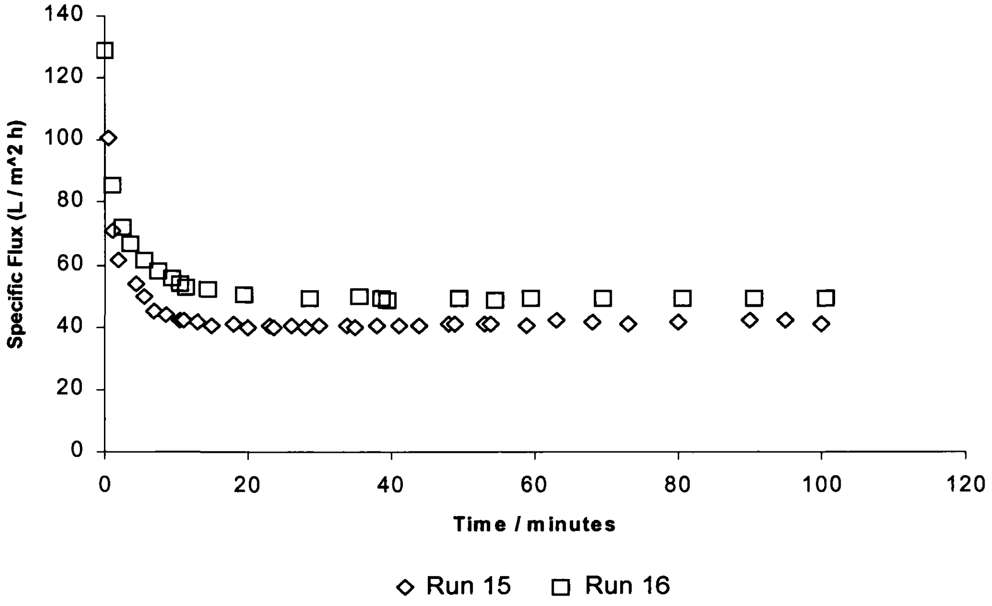


Figure 5-19 Flux Decline during the filtration of "real" emulsion using Tubular PVDF Anionic Membrane under Normal conditions Runs 15 and 16.

Figure 5.20 show the percentage fouling from Runs 15 and 16:

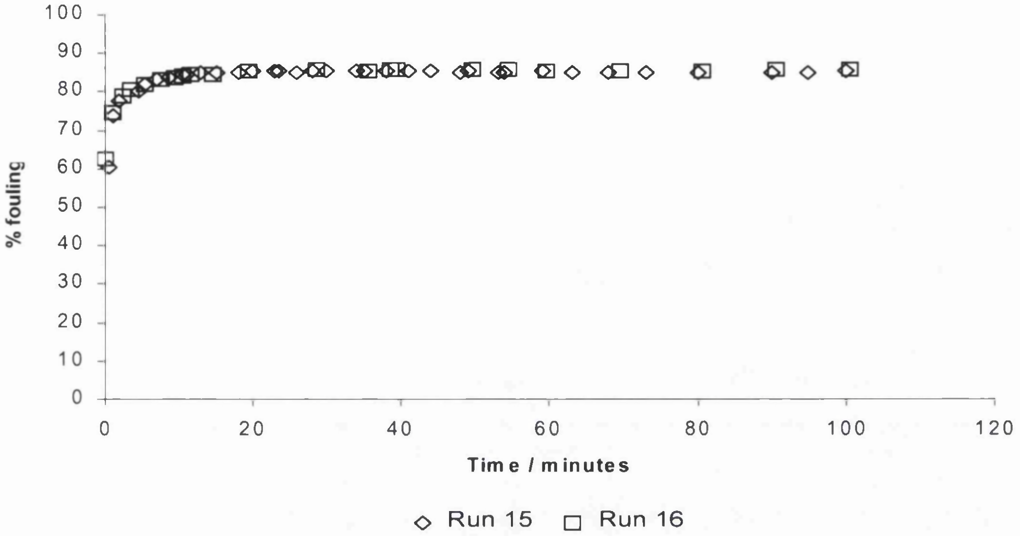


Figure 5-20 Percentage of Total membrane resistance due to fouling of the Anionic Membrane – Normal Conditions Run 15 and Run 16.

Almost identical fouling was observed with both experiments having a final fouling value of 85%. These are higher than the final values reached during the neutral membrane experimental runs under similar pressure and flow rates. Similar final values of fouling suggest that the concentration of oil in the feed does not have a major affect upon the amount of fouling on the membrane.

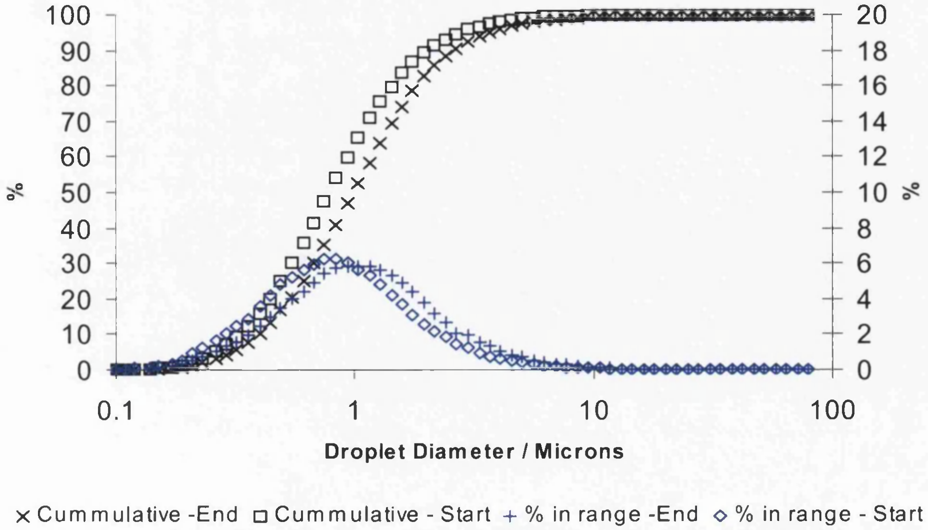


Figure 5-21 Percentage by Volume of Emulsion Droplet Size Distribution for Run 15 Normal Conditions – Start and End.

Throughout both experiments, foaming did occur but only slight signs of free oil were observed. The low value of oil found in both permeates support the lack of free oil in the feed. For Run 15 the droplet size increased slightly over the duration of the experiment and the distribution shape maintained suggesting that the emulsion has remained fairly stable. The change in oil concentration between the start and end also supports this. Comparing the start and end droplet sizes for Run 16, Figure 5.22, a wider distribution of diameters was present in the end feed, increasing the average diameter of the droplet.

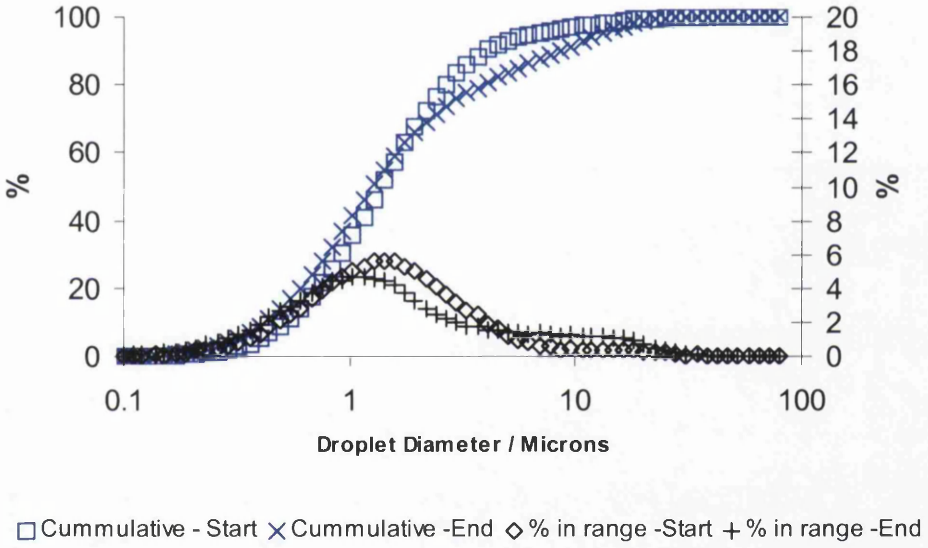


Figure 5-22 Percentage by Volume of Emulsion Droplet Size Distribution for Run 16 Normal Conditions – Start and End.

Variable Pressure (Constant Flow)

Three experiments, Runs 17 – 19, were carried out using the Anionic membrane with a variable pressure and constant flow. As in the previous Variable Pressure filtrations carried out on the Neutral membrane, the first run was carried out using the stop-start technique, with Run's 18 and 19 having the pressure altered immediately without stopping. The following table, Table 5.11, summarises the operating conditions for each run:

Run	Oil Conc. (Start) PPM	Oil Conc. (End) PPM	K μScm^{-1}	pH	Pressure bar	Flow m^3h^{-1}
17	85	73	266	6.1	3.02 – 4.55	1.98
18	225	164	320	6.0	2.98 – 4.49	2.05
19	180	140	237	6.1	1.05 – 2.97	2.06

Table 5-11 Operating conditions for Variable Pressure Filtration using PVDF Anionic Membrane.

Run 17

Again the "stop-start" approach to adjusting the pressure can be clearly seen in the flux graph of Run 17, Figure 5.23:

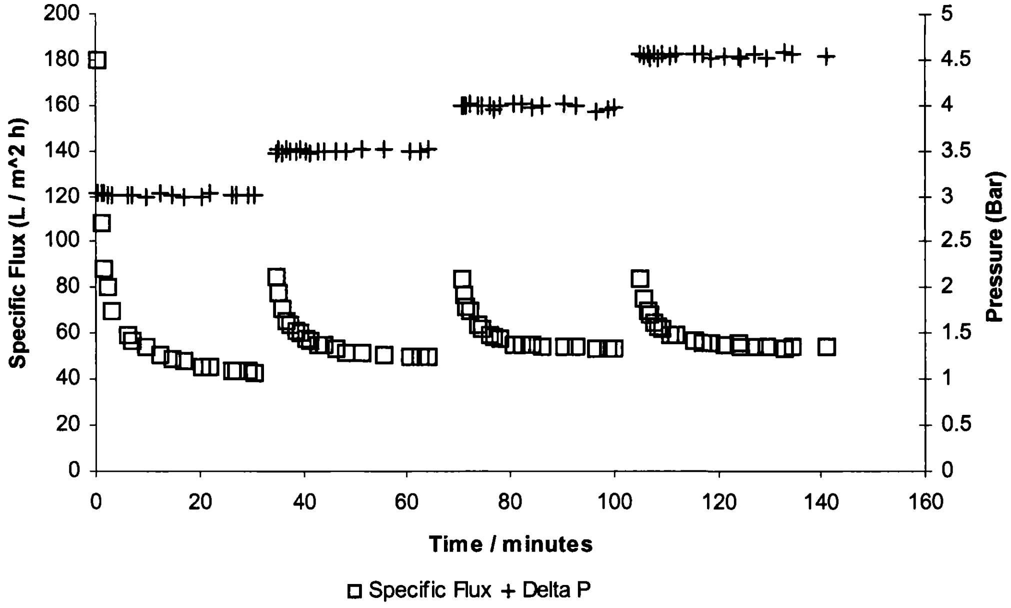


Figure 5-23 Variation in Specific Flux during the filtration of "real" emulsion using Tubular PVDF Anionic Membrane under Variable Pressure conditions – Run 17

The following table summarises Figure 5.23:

Pressure Setting	Average P bar	J initial L m^{-2} h^{-1}	J steady state L m^{-2} h^{-1}	J final L m^{-2} h^{-1}	Time to steady state minutes
P1	3.02	180	45	43	20
P2	3.50	85	52	50	14
P3	3.99	84	55	53	15
P4	4.55	84	55	54	17

Table 5-12 Summary of Flux values observed during the filtration of "real" emulsion using Tubular PVDF Anionic Membrane under Variable Pressure conditions – Run 17 "Stop –Start" conditions.

A high initial flux of ~ 180 L m^{-2} h^{-1} drops by 75% to a steady state value of 45 L m^{-2} h^{-1} after 20 minutes of filtration, this high flux expected due to the low oil concentration. As the pressure was increased, an initial flux increase was observed followed by a gradual decline until steady state was reached. The time to reach steady state increases as the pressure was increased with very little variation in the steady state values at each new pressure. A further decline in flux of ~3-4% was recorded after steady state has been reached at each new transmembrane pressure. A composite permeate sample covering the first two pressure settings had an oil concentration of 5 PPM with the corresponding higher pressure sample containing 10 PPM, producing membrane oil rejection values of 94% and 88% respectively. Slight foaming occurred during the experiment but no free oil was observed. No change in droplet size was observed between the start and end of the filtration.

Run 18

During Run 18 the pressure adjustment was made immediately whilst the pump was still running. In Run 17, after each time the pressure was adjusted, a new high initial flux value was observed. In Run 18 there was no large change in initial flux with each increase in pressure.

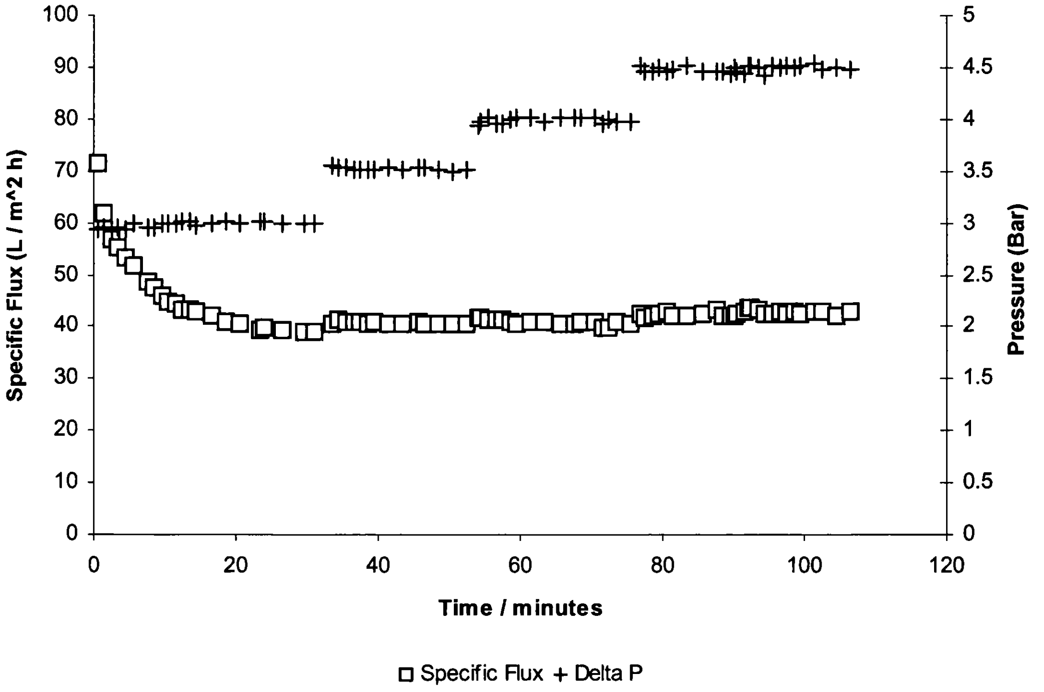


Figure 5-24 Variation in Specific Flux during the filtration of "real" emulsion using Tubular PVDF Anionic Membrane under Variable Pressure conditions – Run 18

An initial starting pressure of 2.98 bar was used, with increases of 0.5 bar made approximately every 30 minutes up to a pressure of 4.49 bar. An initial flux value of 71 L m^{-2} h^{-1} was observed with a decline of 44% to the steady state value of 40 L m^{-2} h^{-1} reached after 26 minutes; with a small further drop in flux to 39 L m^{-2} h^{-1}. As the pressure was increased, an increase of about 1 L m^{-2} h^{-1} in flux was observed. With the final flux value of 42 L m^{-2} h^{-1} being recorded at 4.49 bar.

A composite permeate sample taken during the filtration at the two lower pressures had an oil concentration of 5 PPM, a membrane rejection value of ~98%, with the higher pressure composite sample having an oil concentration of 6 PPM, a membrane rejection of ~98%. Only slight foaming occurred during filtration with no free oil observed in the tank or any change in droplet diameter between the start and end of the experiment as confirmed by Figure 5.25:

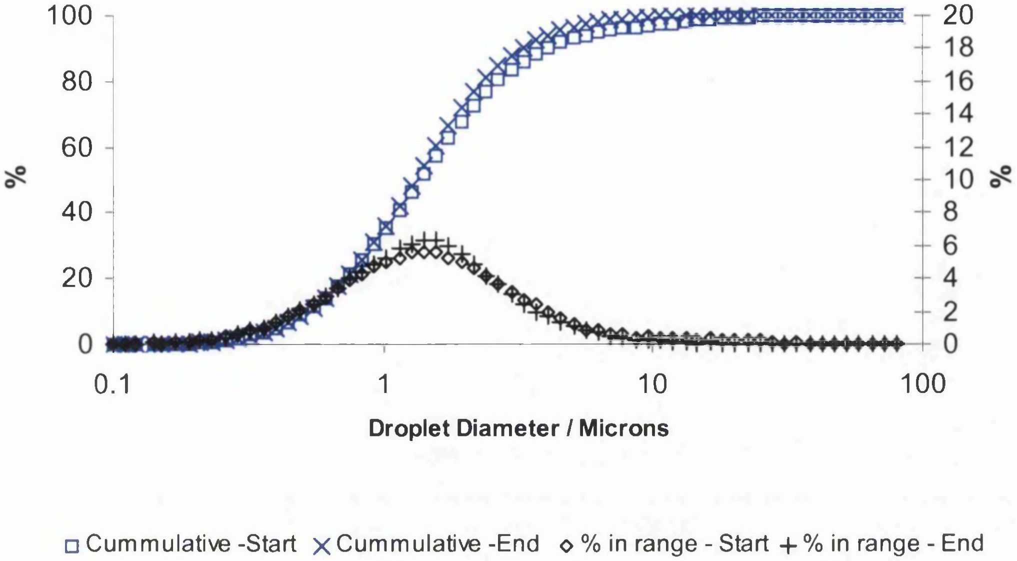


Figure 5-25 Percentage by Volume of Emulsion Droplet Size Distribution for Run 18 Variable Pressure Conditions – Start and End.

Run 19

During this experiment the pressure adjustment was made whilst the pump was running, pressure values ranging from 1 to 3 bar.

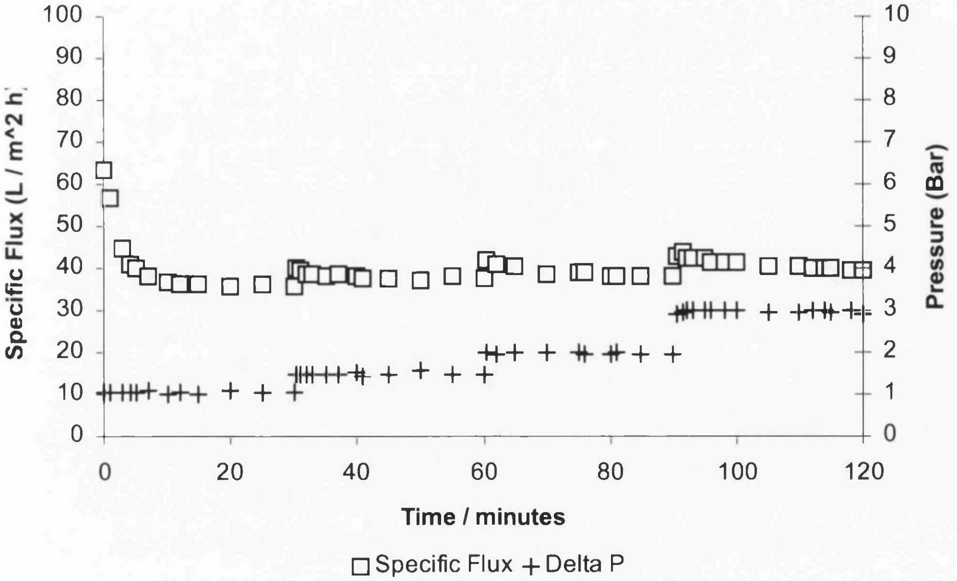


Figure 5-26 Variation in Specific Flux during the filtration of "real" emulsion using Tubular PVDF Anionic Membrane under Variable Pressure conditions – Run 19.

The lower initial flux of 63 L m^{-2} h^{-1} was expected as the initial transmembrane pressure was set low at 1.05 bar. Steady state was reached after 12 minutes of filtration producing a value of 36 L m^{-2} h^{-1} with no further decrease in flux at the initial pressure. The increase in pressure to 1.48 bar produces a slight rise in flux to 40 L m^{-2} h^{-1} but drops to a steady state value of 38 L m^{-2} h^{-1} after ~ 10 minutes, again no further decline in flux was observed. A flux of 42 L m^{-2} h^{-1} was produced at a pressure of 1.98 bar which drops to a steady state value of 39 L m^{-2} h^{-1}, decreasing slightly to 38 L m^{-2} h^{-1}. The final increase to a transmembrane pressure of 2.97 bar brings an initial increase in flux to 43 L m^{-2} h^{-1} which drops to a steady state flux of 41 L m^{-2} h^{-1} after ~ 15 minutes, declining to 40 L m^{-2} h^{-1} by the end of the experiment.

A composite sample of permeate at the two lower operating pressures contained an oil concentration of 5 PPM, a membrane rejection of ~ 97%. A further composite sample from the two higher operating pressures produced an oil concentration of 9 PPM, a membrane rejection of ~ 94%.

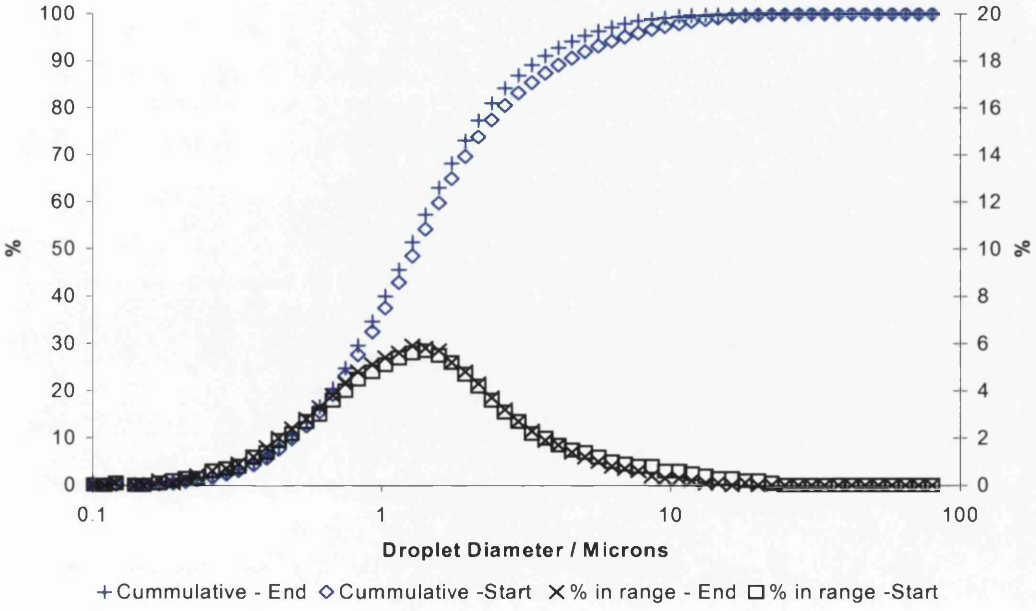


Figure 5-27 Percentage by Volume of Emulsion Droplet Size Distribution for Run 19 Variable Pressure Conditions – Start and End.

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Low oil concentrations in the permeate suggest that no free oil was in the system and Figure 5.27 shows the droplet size distribution of Run 19 with very little variation in droplet size from the start to the end of Run 19. Only slight foaming was observed during this run.

Variable Flow (Constant Pressure)

Two experiments were carried out under variable flow and constant pressure conditions. Table 5.13 summarises the operating conditions:

Run	Oil Conc. (Start) PPM	Oil Conc. (End) PPM	K μScm^{-1}	pH	Pressure bar	Flow m^3h^{-1}
20	393	257	379	5.6	3.48	1.47-3.03
21	605	401	320	5.8	3.59	1.45-2.86

Table 5-13 Operating conditions for Variable Flow Filtration using PVDF Anionic Membrane.

As in previous variable flow experiments, the initial flow was set to the highest flow to be used during the experiment with decreases in flow of ~ 0.5 m^3 h^{-1}.

Run 20

The following table summarises the flux values observed during Run 20 and plotted in Figure 5.28.

Flow Setting	Average Flow m^3h^{-1}	J initial L m^{-2} h^{-1}	J steady state L m^{-2} h^{-1}	J final L m^{-2} h^{-1}	Time to steady state minutes
F1	3.03	102	61	58	12
F2	2.38	55	45	44	11
F3	1.92	43	35	34	18
F4	1.47	32	25	24	21

Table 5-14 Summary of Flux values observed during the filtration of "real" emulsion using Tubular PVDF Anionic Membrane under Variable Flow conditions – Run 20.

An initial flux of 102 L m^{-2} h^{-1} for F1 drops by ~ 41% to a value at steady state of 61 L m^{-2} h^{-1} after 12 minutes, with a further decrease to 58 L m^{-2} h^{-1}. As the flow was decreased, the flux values drop and a new steady state value being obtained each time, with an increase in the time taken to reach steady state.

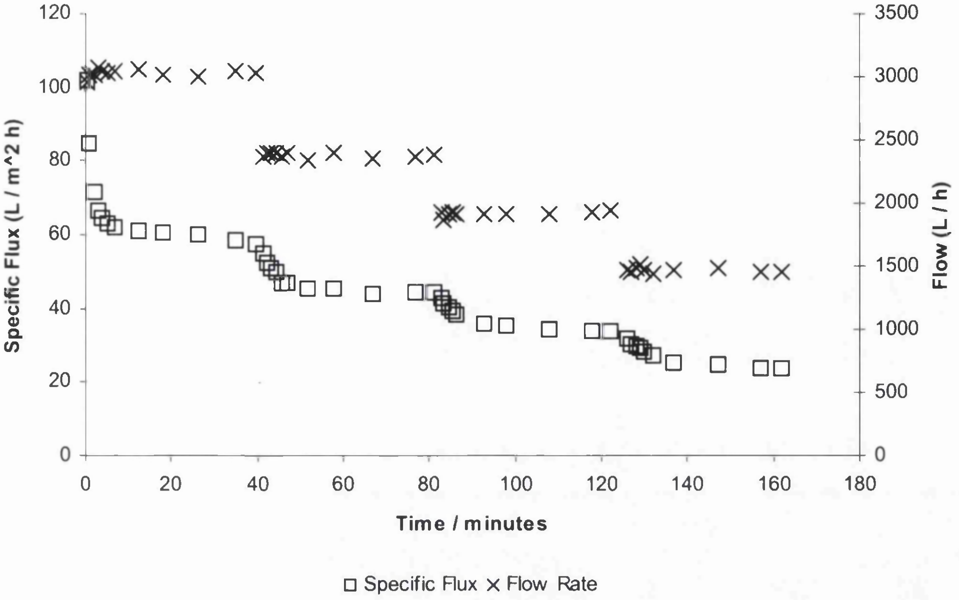


Figure 5-28 Variation in Specific Flux during the filtration of "real" emulsion using Tubular PVDF Anionic Membrane under Variable Flow conditions – Run 20.

The permeate sample had an oil concentration of 5 PPM, a membrane rejection of ~ 98% and an iron content of 7.3 PPM. A small amount of foaming was observed but there was no effect on the droplet size, see Figure 5.29, suggesting that the emulsion remained stable.

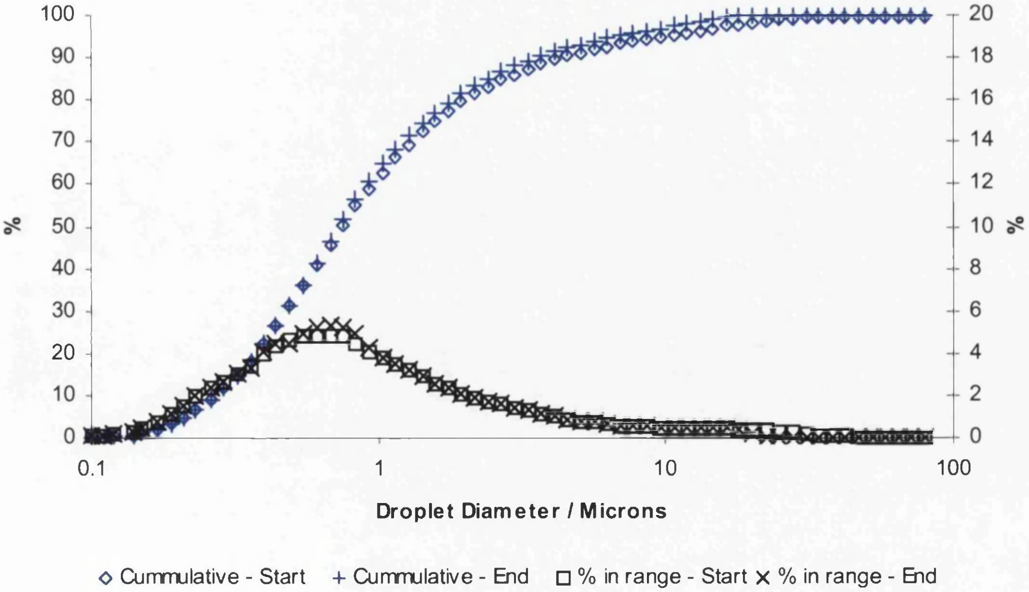


Figure 5-29 Percentage by Volume of Emulsion Droplet Size Distribution for Run 20 Variable Flow Conditions – Start and End.

When comparing the flux between variable flow conditions to one obtained under constant operating conditions, the variable conditions tend to reduce the expected flux.

Run 21

The flow during Run 21 was varied between ~3 and 1.5 m3h^{-1}. see Table 5.15. An initial flux value at F1 of 81 L m^{-2} h^{-1} dropped by ~ 27% to a steady state value of 59 L m^{-2} h^{-1} with no further decrease at this flow setting. Although a low drop in initial flux, the time taken to reach steady state was similar to many of the previously reported experiments. Further drops in flux and steady state values are reported after each change in flow, with an increase in the time taken to reach a new steady state.

Flow setting	Average Flow m^{3}h^{-1}	J initial L m^{-2} h^{-1}	J steady state L m^{-2} h^{-1}	J final L m^{-2} h^{-1}	Time to steady state minutes
F1	2.86	81	59	59	11
F2	2.50	57	52	52	10
F3	2.03	50	43	42	16
F4	1.45	40	29	29	23

Table 5-15 Summary of Flux values observed during the filtration of "real" emulsion using Tubular PVDF Anionic Membrane under Variable Flow conditions – Run 21.

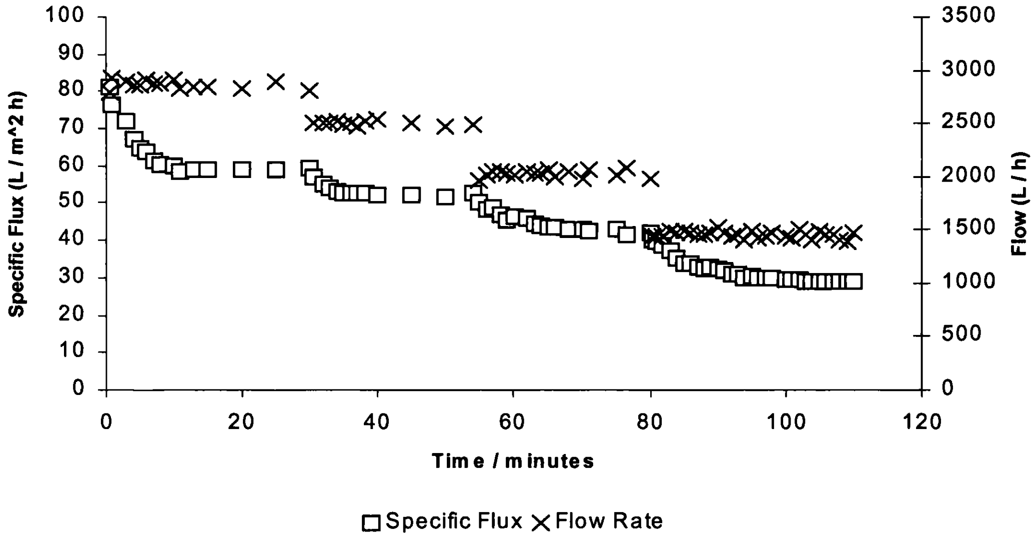


Figure 5-30 Variation in Specific Flux during the filtration of "real" emulsion using Tubular PVDF Anionic Membrane under Variable Flow conditions – Run 21.

Droplet diameter increased from start to end of the experiment, with a tighter distribution around 2 microns suggesting that smaller droplets were coalescing. The fact that no further decrease in flux was observed once steady state had been reached could be due to the presence of larger droplets and a looser packing in the fouling layer, countering the expected progressive increase in fouling.

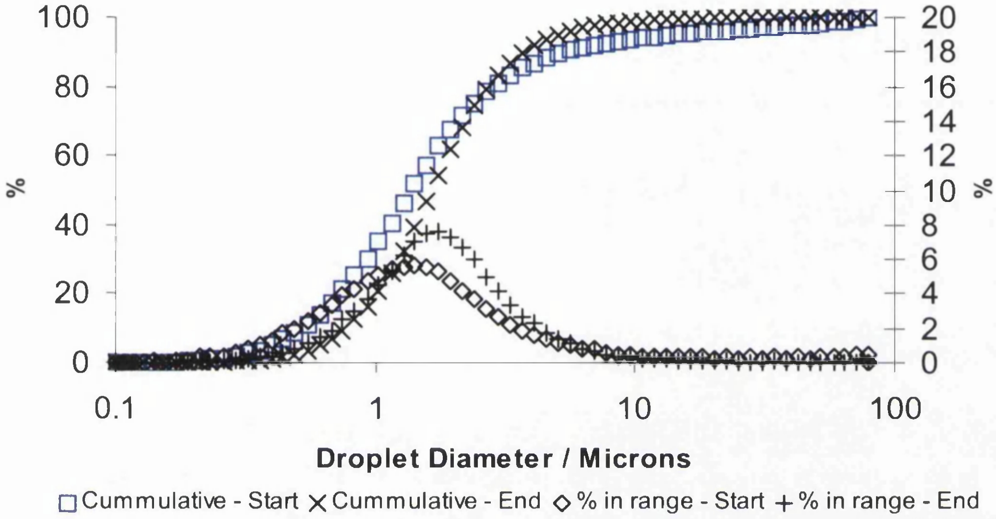


Figure 5-31 Percentage by Volume of Emulsion Droplet Size Distribution for Run 21 Variable Flow Conditions – Start and End.

A composite sample of permeate obtained for the two initial flow settings contained 6 PPM oil, a membrane rejection of ~ 99%, and a further sample obtained over the last two flow settings contained 8 PPM oil, a membrane rejection of ~ 98%. Both samples contained levels of iron, 19.9 and 19.2 PPM respectively. Despite the high concentrations of iron found in the permeate, the flux values obtained during the filtration were high. Slight foaming was observed with minimal free oil on either the sides of the feed tank or on top of the foam.

The following Figure 5.32 compares the fouling of the membrane during Run's 20 and 21 under variable flow-constant pressure:

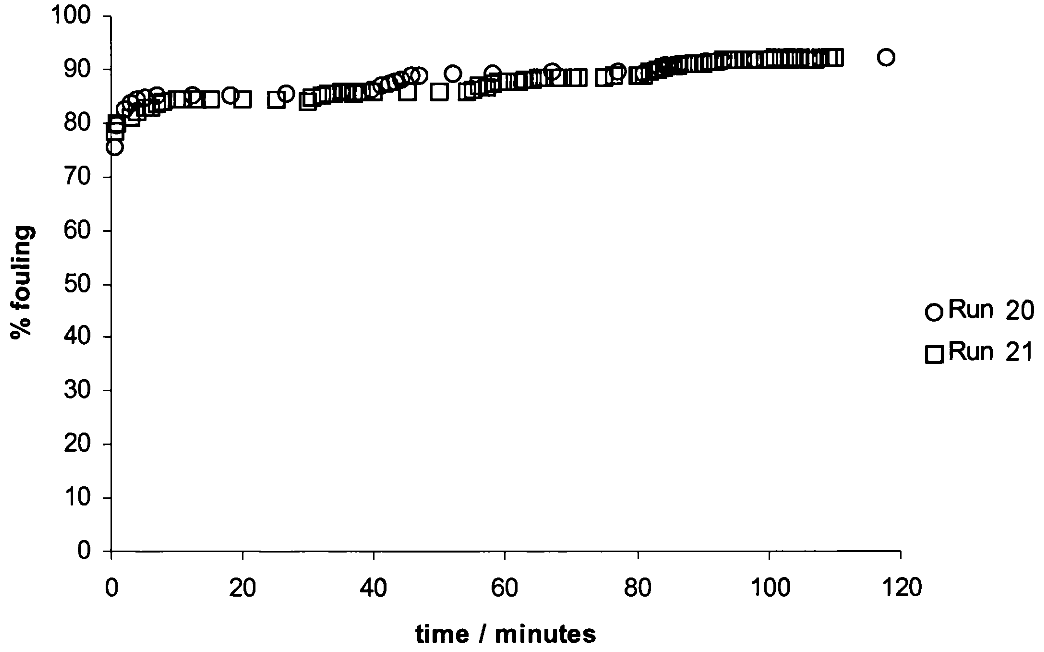


Figure 5-32 Percentage of Total membrane resistance due to fouling - Anionic Membrane under Variable flow and constant pressure.

Almost identical amounts of fouling are observed for both runs, with final values of 92%. The fouling increases with time, corresponding to the drops in flow rate showing that the amount of fouling was dependant upon feed flow rate. This was in contrast to the Neutral membrane, see Figure 5.13 and Figure 5.18, with very clear changes in percentage due to fouling of the total membrane resistance.

5.4.4 Hollow Fibre PAN

Three Initial Runs were carried out that looked at the general filterability of the emulsion based around the recommended operating conditions. No sizing experiments were carried out for these runs and only the basic analysis was carried out. The data-logger recorded data every eight seconds and the flow and pressure was set as described in Chapter 4.3.2 Flow and Pressure Setting, also allowing for temperature stabilisation. Permeate sampling was undertaken as described in Chapter 4.3.5 Permeate Measurement and Sampling. During these initial experimental runs, the permeate was collected therefore increasing the concentration of the oil in the feed tank.

Run Number	delta P bar	Actual flow $m^3 h^{-1}$	cross flow velocity $m s^{-1}$	Reynolds Number (in fibre)	Permeabilty J / P Start	Permeability J / P End	Feed Oil conc mg / L	Permeate Oil con mg / L	flux start $L / m^2 h$	flux finish $L / m^2 h$	% drop	Volume Permeate collected L	Duration minutes
Run 22	1.87	3.755	1.74	2169	16.6	1.9		11	30.05	1.06	96	61.5	370
Run 23	1.87	3.824	1.77	2212	24.92	8.2		10	43.3	15.6	64	57.5	120
Run 24	1.88	3.802	1.76	2199	33.28	17.3		10	58.9	33	44	53.5	60

Table 5-16 Operating conditions for Initial filtration Runs using PAN Hollow Fibre membrane – Permeate collected during filtration.

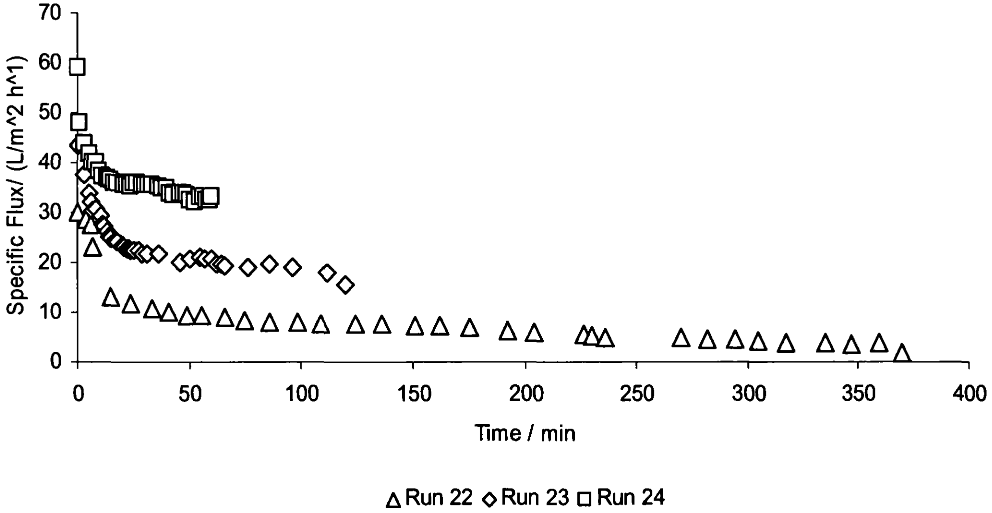


Figure 5-33 Flux graph for PAN Hollow Fibre Initial Filtration Runs 22 – 24 – Permeate collected during filtration.

Normal Operating Conditions

Four experiments were carried out using the PAN membrane, two under "normal" conditions and one of each under variable flow and constant pressure and variable pressure and constant flow. The operating conditions for the experiments are summarised in Table 5.17:

Run	Oil Conc. (Start) PPM	Oil Conc. (End) PPM	K μScm^{-1}	pH	Pressure bar	Flow m^3h^{-1}
25	369	301	289	6.1	1.83	3.99
26	316	281	267	5.7	2.03	3.93
27	103	88	278	6.1	1.46 – 2.68	3.71
28	387	217	379	5.6	1.91	1.92 – 4.74

Table 5-17 Actual Operating conditions for filtration using PAN Hollow Fibre Membrane.

The operating flow rate recommended by Koch was twice that of the Tubular PVDF membranes, 4 m^3h^{-1} compared to 2 m^3h^{-1}. The individual fibre diameter was 1.1 mm compared to the diameter of the tubular membranes of 25.4 mm. These experiments allowed the comparison of different module formats when treating the waste emulsion. The hollow fibre is a high flow – low pressure membrane with a large surface area packed into a small module footprint. The following Figure 5.34 is the flux graph for Run's 25 and 26.

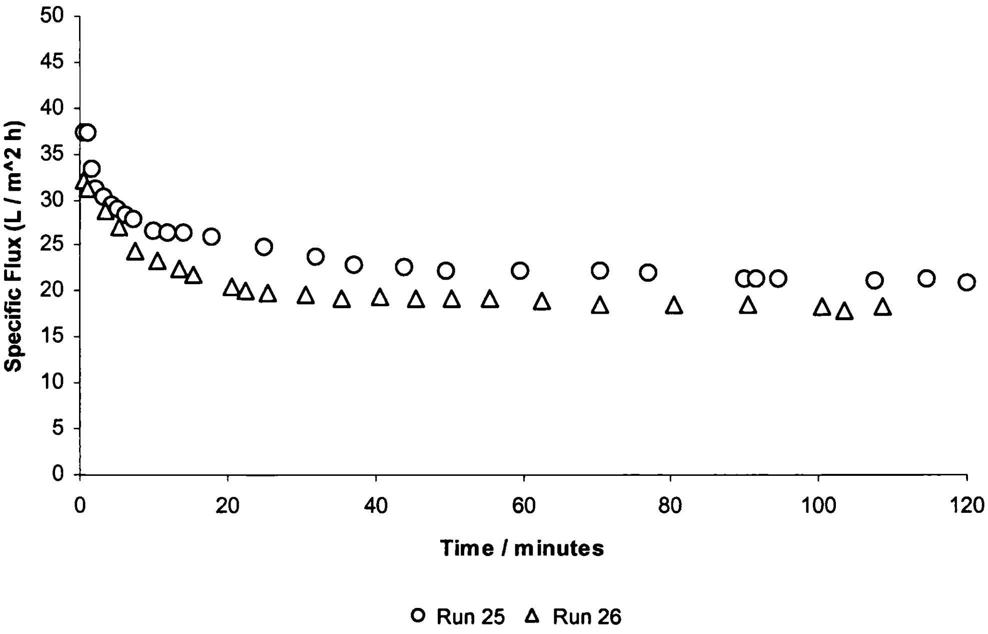


Figure 5-34 Flux decline during the filtration of "real" emulsion using a Hollow Fibre PAN Membrane under Normal conditions – Run 25 and Run 26

The initial flux for Run 25 was 37 L m^{-2} h^{-1} with steady state reached after 10 minutes, with a flux value of 26 L m^{-2} h^{-1}, a drop of 30%. The flux continues to drop off with the development of another steady state developing after ~ 60 minutes with a value of 22 L m^{-2} h^{-1} dropping gradually to a final flux of 21 L m^{-2} h^{-1}. Run 26 follows a more expected pattern of the high initial flux, 32 L m^{-2} h^{-1}, dropping to a steady state value of 19 L m^{-2} h^{-1} after 40 minutes corresponding to a drop in flux of 40% of the initial value. Further flux decline was observed with a final flux value of 18 L m^{-2} h^{-1}.

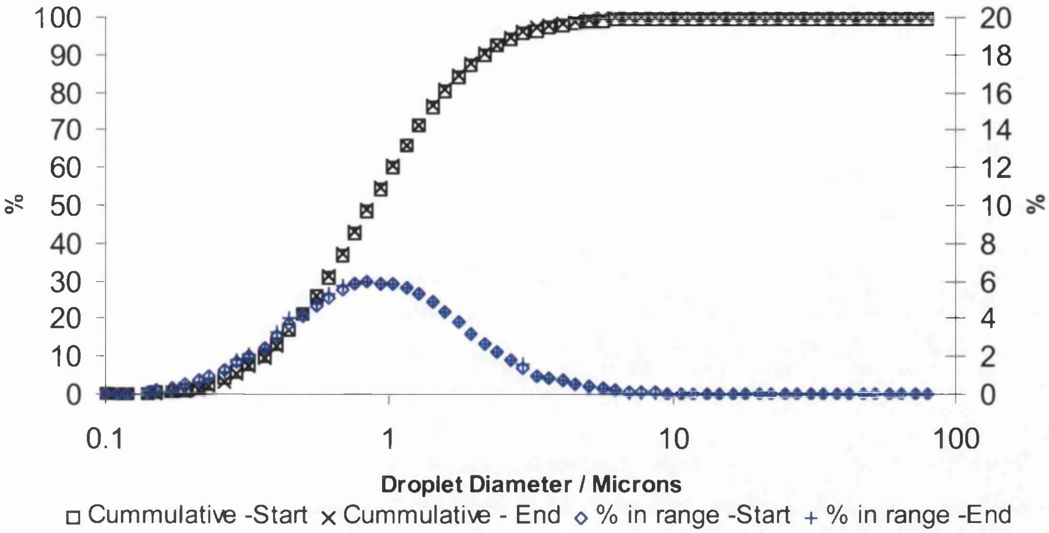


Figure 5-35 Percentage by Volume of Emulsion Droplet Size Distribution for Run 25 Normal Conditions – Start and End.

There was no variation in droplet diameter from start to end of the filtration for Run 25 with similar results for Run 26, as shown in Figure 5.35. During both experiments, minimal foaming was observed even though the flow rate was higher than previous filtrations. This was possibly due to the fact that at this flow rate, a more developed flow after valve V3 was observed exiting the return pipe to the feed tank, resulting in a less ferocious mixing. No free oil was observed in the system and the permeate samples for Run 25 contained 9 PPM of oil and Run 26 contained 6 PPM of oil.

Despite Run 25 having a lower operating pressure, higher flux values were observed. Plotting the percentage fouling against time, Figure 5.36, which takes into account the pure water flux measured before the experiment into consideration, slightly more fouling occurred compared to Run 26. This could be due to the PWF of Run 25 being ~110 L m^{-2} h^{-1} and Run 26 being substantially lower, ~ 80 L m^{-2} h^{-1}. When the percentage fouling was calculated, the clean membrane resistance was lower for Run 25 so that any difference in flux has a greater impact on the total resistance of the membrane. This paradox of a higher flux actually corresponding to a higher fouling percentage highlights the importance of sufficient cleaning of the membrane to maximise operating fluxes.

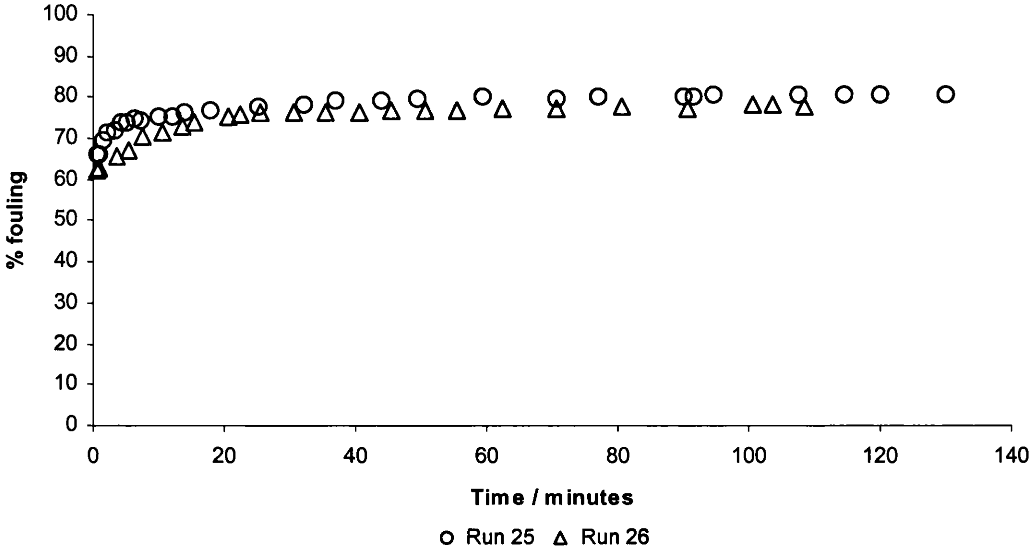


Figure 5-36 Percentage of Total membrane resistance due to fouling - Hollow Fibre at Normal Conditions Run 25 and Run 26.

Variable Pressure (Constant Flow) – Run 27

One experiment was carried out under variable pressure and constant flow conditions. In this experiment, the pressure was adjusted instantly whilst the system was running. The experiment used the pressure range of 1.46 to 2.68 bar compared with the recommended pressure 2 bar by Koch. The pressure was not altered drastically outside of the recommended pressure due to the lack of data on the membrane modules safe operating pressure range. The following Figure, 5.37, shows the flux graph:

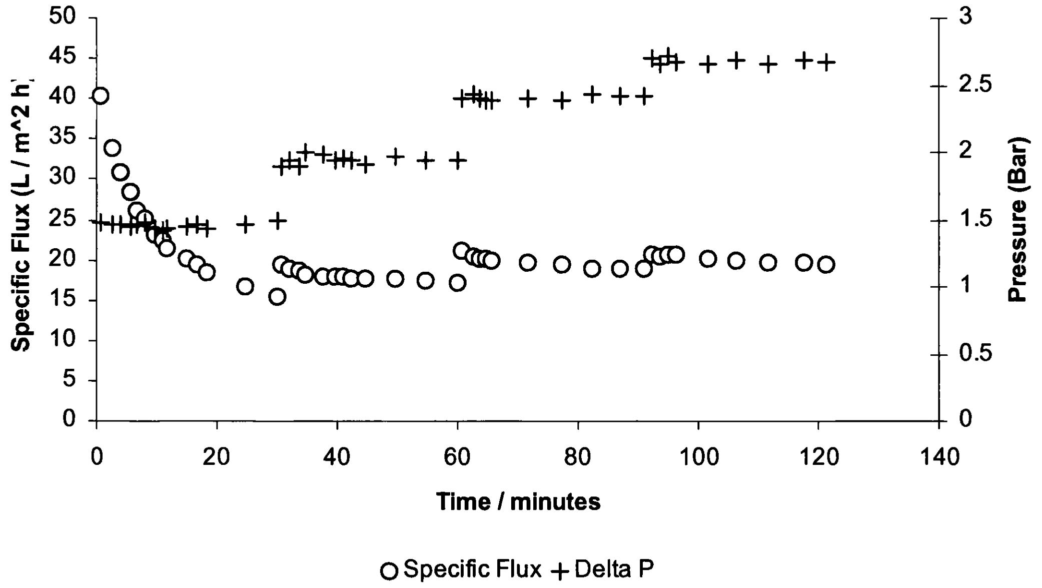


Figure 5-37 Variation in Specific Flux during the filtration of "real" emulsion using Hollow Fibre PAN Membrane under Variable Pressure conditions – Run 27.

The following table summarises Figure 5.37:

Pressure Setting	Average P bar	J initial L m^{-2} h^{-1}	J steady state L m^{-2} h^{-1}	J final L m^{-2} h^{-1}	Time to steady state minutes
P1	1.46	40	Not reached	15	> 30
P2	1.94	19	18	17	10
P3	2.41	21	19	19	22.5
P4	2.68	21	20	19	15

Table 5-18 Summary of Flux values observed during the filtration of "real" emulsion using Hollow Fibre PAN Membrane under Variable Pressure conditions Run 27.

An initial flux of 40 L m^{-2} h^{-1} was measured and despite the experiment being ran for over 30 minutes, the steady state flux had not been reached. The final flux measured at P1 was 15 L m^{-2} h^{-1}, a drop of ~ 63% from the initial flux. As the pressure was increased, the flux also increases, with the initial flux value of P2 being noticeably higher than the final value measured for P1.

At P2, the expected drop in flux occurs as the experiment progresses, with steady state flux producing a value of 18 L m^{-2} h^{-1} and a final value of 17 L m^{-2} h^{-1}. With each further increase in pressure, the flux also increases with little or no further decrease with time. The time taken to reach steady state increases from P2 to P3 but decreases with the transition from P3 to P4. This could be due to the membrane already experiencing substantial fouling and the further increase in pressure was not significant enough to increase the flux even temporarily. As in the Run 25 and Run 26, no change in droplet diameter showing similar results to Figure 5.35. Minimal foaming occurred with no free oil in the system. The final flux value was low despite having a low oil concentration in the feed. Two composite samples were taken of the permeate, with both samples containing 13 PPM of oil.

Variable Flow (Constant Pressure) – Run 28

One experiment was carried out under variable flow and constant pressure. Each change in flow was made instantly whilst the system was running. The flux graph is presented in Figure 5.38. An initial flux of 25 L m^{-2} h^{-1} drops by 32% to a steady state value of 17 L m^{-2} h^{-1} reached after 36 minutes. As the flow was reduced, the drop in flux was slight with no readjustment from a significant drop in flux to a new steady state as seen in all other variable flow – constant pressure experiments. The final flux value of 14 L m^{-2} h^{-1} recorded at a flow rate of 1.92 m^3 h^{-1}. Permeate contained 8 PPM of oil, a membrane rejection of 97 %.

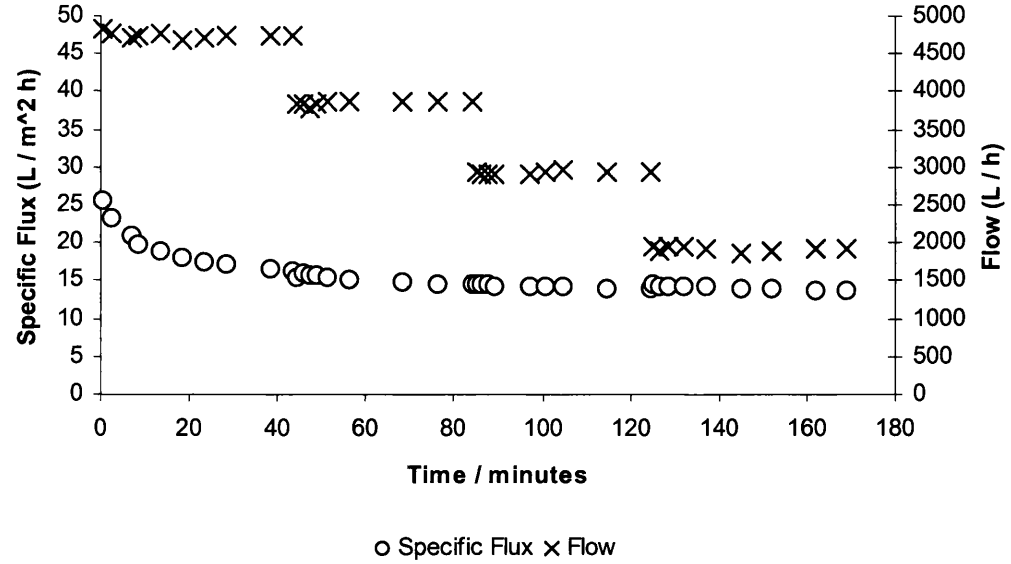


Figure 5-38 Variation in Specific Flux during the filtration of "real" emulsion using Hollow Fibre PAN Membrane under Variable Flow conditions Run 28.

When looking at the fouling graph for the experiment, see Figure 5.39, the expected high values of fouling are not seen. The final percentage fouling value of 80% was similar to other experiments.

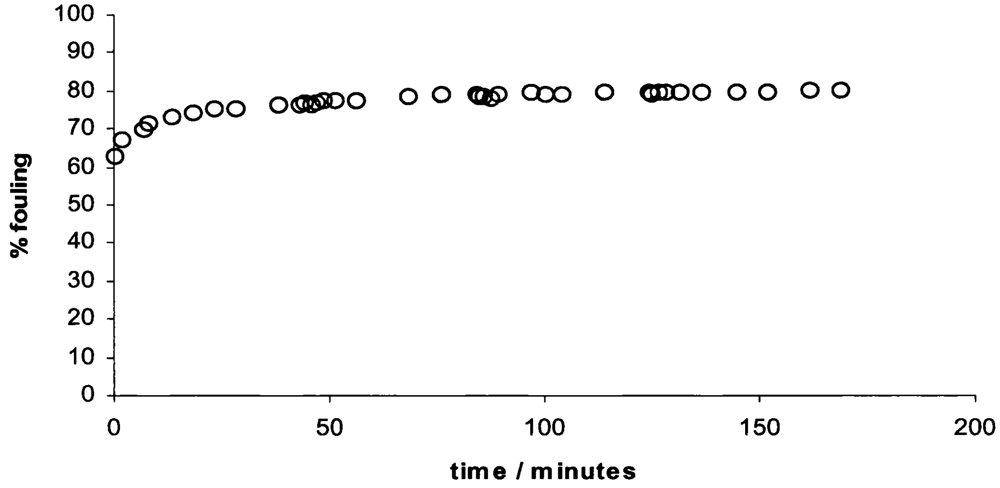


Figure 5-39 Percentage of Total membrane resistance due to fouling Variable flow (Constant Pressure) Run 28 – Hollow Fibre.

5.5 Cleaning

The membrane was benchmarked before each experimental run using double distilled water to calculate the resistance of the clean membrane. Before the membrane was cleaned, the membrane was removed from the system and the rig was drained and cleaned as detailed in Chapter 4.3.4. Cleaning the membrane was undertaken using an alkaline-acid-alkaline wash cycle as suggested by [86] and using the principles suggested by [109], with rinsing using double distilled water in between of each cycle to remove any previous cleaning solution.

There were several different stages to membrane cleaning. For the first alkaline rinse, the operating pressure was kept relatively low to around 2 bar for the PVDF tubular and 1.25 bar for the PAN hollow fibre with a flow rate of 2 $m^3 h^{-1}$ for both. An alkaline dishwasher cleaner was used at a typical concentration of 1.5 g / L into double distilled water with a pH of around 10 and temperatures of 23 – 25 °C.

When the pump was started to circulate the cleaning solution, the first ~2 litres was collected as this first flush can contain quite large concentrations of oil and other foulants. This action minimised the amount of oil / foulants that can potentially be re-dissolved and re-foul the membrane. The cleaning solution was circulated for between 20 – 25 minutes with the permeate valve shut. After this initial period, the permeate valve was opened and the operating pressure increase by ~ 1 bar to 3 bar for the PVDF but remaining the same for the PAN. The cleaning solution was circulated for a further 15 minutes to clean through the pore structure of the membrane. The flux can be measured at this stage and used as an indication to how successful the cleaning has been thus far.

The rig was then stopped and drained of the alkaline cleaning solution, normally now brown-grey in colour and with some large trapped bubbles with an oily film. The membrane was removed and the appropriate blank placed in to complete the rig. The rig was then cleaned as described in Chapter 4.3.4. This rig cleaning procedure can be reduced if the operator feels that there was minimal problem with residual solution and then a quick rinse was undertaken of the rig and drained. The membrane was then replaced and rinsed with double distilled water to remove any alkaline traces.

A citric acid solution was then made up from powered citric acid, supplied from Fisher Scientific, Uk, and double distilled water at a concentration of 15 g / L of water given a typical pH of 2.5. The acid cleaning run was undertaken using the normal operating conditions recommended by the membrane manufacturer for 15 minutes with the permeate valve shut for the first ten minutes of operation and then opened for the last 5 minutes. The rig was then drained and cleaned as described in Chapter 4.3.4 with the same operator discretion as before.

The membrane was then rinsed with double distilled water and the PWF measured under normal operating conditions. Depending on the value of the PWF compared to that measured before the experiment, a further alkaline cleaning stage was undertaken. If this were required, a 0.01 M Na OH solution would be made up using Na OH pellets, Fisher Scientific, Uk and double distilled water having a typical pH of 11 –12. This would operate under normal conditions and last for up to 20 minutes and with permeate flowing throughout the run. The flux was measured every couple of minutes and this used to decide whether or mot to continue with the cleaning. Values measured here were normally at lest 90 – 95% of the expected PWF. In some cases for persistent fouling, the Na OH cleaning solution would be heated to temperatures around 35 °C but this not very common.

During the cleaning of the PAN membrane, the critic acid had a negative effect on PWF and rendered the membrane seriously fouled. This restricted the number of experiments that used the PAN membrane and hence only four experiments were conducted using this filter. Repeated efforts using various concentrations of alkaline cleaners and temperatures were used in an attempt to recover the flux but were not successful. This was unexpected behaviour as the authors of [86] used a similar cleaning cycle for a PAN membrane with their citric acid rinse corresponding to a pH of 1.4, slightly more acidic than the concentration used during my citric rinse. The authors report effective cleaning of the PAN membrane using the alkaline-acid-alkaline rinse.

For both the PVDF membranes, the use of the first alkaline rinse produced similar recoveries in flux. In general, the anionic membrane responded better to the use of citric acid compared to the neutral membrane with the previously reported negative impact on the PAN. During the acid rinse using the anionic membrane, a slight acidic fume was given off.

As the experimental scheme was undertaken, a drop in pure water flux after cleaning was noted, suggesting that the membrane was becoming progressively permanently fouled.

5.6 Discussion

5.6.1 General Filterability

Twenty-eight experiments were undertaken using a sampled waste emulsion and produced a consistently high quality permeate with regards to oil concentration and suspended solids. In all cases, the permeate was within the limits being proposed for controlling discharges from the Metal Products and Machinery Sector in America, [24]. The flux values quoted in [24] for Koch's Tubular membrane at 25°C and 3.5 bar are 50 $L\ m^{-2}\ h^{-1}$, this was slightly higher than the values obtained under the normal operating conditions used for the PVDF membranes, i.e. an average of 38 $L\ m^{-2}\ h^{-1}$ and 45 $L\ m^{-2}\ h^{-1}$ for the Neutral and Anionic Membrane respectively. In [108] typical flux values were 46 $L\ m^{-2}\ h^{-1}$, using a longer module of ten feet and using a prepared emulsion. Values from [92] for membranes of different materials are also in these ranges treating a spent emulsion from ships.

Sampling was carried out over several months, covering changes in production rates and general differences due to possible weather effects, varying degrees of emulsion stability and concentration. The membranes were able to handle the wide variety of the effluent produced by the cold mill, proving that the membranes are a robust treatment process. This suggests that feed concentration over the ranges used during the experiments was not a major factor in the membrane treatment of waste emulsion also supported by [92]. The initial Runs 1 – 6, with the exception of Run 2 and 3, did not show a substantial decrease in specific flux even though the feed concentration had doubled due to the collection of the permeate. The experiments were carried out over 5 hours and indicated that the operating flux over time would remain between 40 – 60 L m^{-2} h^{-1}.

The quality of permeate produced was suitable for further use within the steel works. Several authors, [91-92] report on the use of combined UF / RO plants producing consistently high quality water suitable for direct discharge to a sewer or considered for reuse. This combination would be of interest due to the relatively low conductivity of the feed and the removal of all suspended solids, making it an ideal feed to an ULPRO plant. The site already has a large demand for de-ionised water and the security of supply to the demineralised facility is one of an ongoing concern although the maximum flow rates through this plant are low compared to this demand.

5.6.2 Effect of Feed Flow Rate

For both the tubular membranes, a high flow rate had a positive effect on the flux. This is typical behaviour due to the effect of higher flow corresponding to a higher shear rate over the membrane surface and was reported by many authors. For each change in flow rate, a new equilibrium was achieved as the fouling layer re-adjusts to the flow conditions, with marked drops in flux for each new flow rate. The final flux values drop by an average of ~ 60% from the high starting flow rates to the final low flows. This was the same for both the Neutral and Anionic membrane suggesting that the surface charge has little affect when using flow to minimising fouling. With each change in flow rate, the transient period between the initial flux and the steady state flux for each new flow rate increased as the flow was reduced. This corresponds to each new equilibrium taking longer to readjust to the flow conditions due to the reduction in shear at the membrane – fouling interface.

In all three of the Neutral membrane runs (Runs 12-14) under variable flow, the flux value measured at a flow corresponding to "normal" conditions was less than the average flux value recorded under "normal" operating conditions. This suggests that a greater extent of fouling occurred earlier during the experiments due to the higher fluxes bringing more fouling components to the membrane surface. The fouling was being controlled by the high shear but once this dropped to normal levels, resultant fouling increased to levels greater than expected, (this was only true for Run 20 of the Anionic Variable flow experiments).

Comparing the amount of fouling for each membrane under the variable flow conditions, there was only a slight increase from start to end for the anionic membranes whereas the neutral membrane increased from initial values of ~ 60% to final values of between 85 and 91%, showing a large dependence upon cross flow. In general, the final percentages of total membrane resistance due to fouling were higher for the anionic membrane, suggesting that the neutral membrane was more resistant to fouling. The lower rate of fouling for the neutral membrane also confirms this.

Another effect of operating at higher flow rates was the change in pressure drop along the membrane module at a given pressure. At the typical pressure of 3.5 bar, the pressure drop along the membrane, measured via the pressure transducers at either end of the membrane, showed an increase with an increase in flow rate. Flow rates of 1000 L /h typically resulted in a pressure drop of 0.13 bar increasing to values > 0.22 bar at pressures around 4-4.5 bar. The effect was present for both tubular membranes and will affect the energy consumption during filtration as well as localised effects along the length of the membrane.

5.6.3 Effect of Transmembrane Pressure

During Run 9 (Neutral) and Run 17 (Anionic), the increased pressure was applied by initially stopping the filtration, setting the new pressure and then restarting the filtration. This resulted in a noticeable increase in initial flux after each new pressure with a drop to a new steady state slightly greater than the previous steady state value. The initial increase in flux was attributed to the relaxing in pressure and hence the force holding the fouling layer onto the membrane surface. In a review of additional techniques to improve microfiltration [85], it was reported that pulsation of the flow was one method that can have an effect on the concentration polarisation layer due to the change in hydrodynamic conditions. The stop-start approach of the experiment and the resulting flux increases confirms the possibility that this technique was useful for prolonging the time required between cleaning cycles. It was noted in the paper that the techniques are applicable to both microfiltration and ultrafiltration.

Overall for the tubular membranes, an increase in pressure after an initial steady state had been reached resulted in little or no gain in flux. This apparent independence of flux with pressure could be due to the operating pressure being in the pressure independent region for the solution or that the fouling layer forms very rapidly. This suggests that thickness of the gel concentration was such that its resistance was greater than the total resistance of the membrane. The only way to therefore increase the flux would be reduce the gel polarisation layer, possibly by turbulence. The higher pressures used could have also caused oil droplets to enter the membrane pores. The presence of oil in the pores resulting in effective pore blocking resulting in a drop of flux for the effected pores countered by an increase in flux for the unaffected pores.

This was hard to verify as there was no large increase in oil concentration of the permeate during these experiments.

For Run 11 (Neutral membrane), the pressure range covered for the experiment was from one bar to a final pressure of three bar. During this experiment there was a more marked change in flux as the pressure was increased. Although small, the noticeable increase suggests that the flux was not completely independent of pressure and that the membrane was being operated in the range where the resistance of the gel layer was << than the total membrane resistance.

5.6.4 Effect of Surface Charge

In overall terms, the anionic membrane produced higher flux values in the majority of experiments. This could be attributed to the higher resistance of the membrane to become "wetted" by the oil in the feed. Before each experiment the pure water flux was measured for each membrane and in all the cases the PWF of the anionic membrane was higher, resulting in a lower clean membrane resistance. Looking at the pure water flux experiments, the Anionic membrane showed a reduction in flux with time when compared to the consistent flux values produced by the Neutral membrane. The reduction flux being attributed to the swelling of the hydrophilic anionic membrane, see [87]. This was typical behaviour when comparing charged and non-charged membranes.

When looking at the flux decline patterns for each waste emulsion experiment type, there was no clear distinction between the different surface charges. It was only when comparing the fouling graphs that take into account the clean membrane resistance are you able to see the actual effect of the filtration on the membrane surface.

The anionic consistently showed higher percentage fouling throughout even though the flux values being measured were higher than those for the neutral membrane. When the membranes were cleaned after an experiment, the anionic was generally easier to clean and required less severe or repeated cleaning measures. The measure of the effect of cleaning was the value of the PWF obtained after "regular" cleaning. It was in this area where the surface charge of the membrane could play a larger part as the cleaning agents used were alkaline cleaning solutions combining non-ionic and ionic surfactants.

The PWF recorded before each experiment gradually decreased with time for both tubular membranes. Over the period of waste emulsion filtration, with varying levels of cleaning, the PWF of the Anionic membrane had dropped by about 21% and over the same period of time, the neutral membrane PWF had dropped by about 35%.

In all cases, the membrane was cleaned until the PWF recorded was of a value similar to that obtained before the experiment. If this point was not reached, cleaning severity was increased. This normally meant that sodium hydroxide was added to the standard alkaline cleaning solution. The ease by which the anionic membrane was cleaned and the overall higher fluxes would have a major bearing on what membrane would be employed in a full-scale treatment plant. The ability of the anionic membrane to retain its PWF over time would suggest that this was the membrane of choice for a full-scale plant.

5.6.5 Hollow Fibre Membrane

Overall, the permeate produced by the PAN membranes was of a high standard, the maximum value for the 7 experiments was 13 PPM. In the case of the variable flow run, excessive cleaning was required afterwards to restore the PWF. Flux values measured during the experimental runs are similar to ranges given for a PAN membrane with a MWCO of 70 000 [92].

Normal Conditions

Comparing Run 25 and Run 26 for the filtration of waste emulsion under normal conditions; a difference in flux pattern was seen even though both experiments are using similar feeds. The lower pressure of Run 25 results in a higher flux at both steady state and at the end of the experiment. This suggests that Run 26 experienced more compaction of the fouling layer at the higher pressure than any other benefits from an increased driving force.

This was not unusual in membrane filtration especially in the area of deformable particles. The slower rate to reach steady state by Run 26 was expected due to the higher pressure and similar results have been reported by Wakeman and Tarleton [111] albeit over larger pressure differences than those between Run 25 and 26. Similar amounts of fouling for both runs was seen, with Run 25 having slightly more fouling due to the higher fluxes bringing more fouling material to the membrane. The PWF of Run 25 was also substantially higher, indicating the importance of cleaning on fluxes attained immediately after.

Variable Pressure (Constant Flow) – Run 27

At the low initial pressure during Run 27, the steady state was not reached even after 30 minutes of operation. At this lower pressure, a lower driving force brings emulsion to the membrane surface at a slower rate, so that the time taken to reach steady state was increased. This was further amplified by the lower oil concentration in the feed. As the pressure was increased by approximately 0.5 bar intervals, the initial flux increases markedly up until 2.41 bar after which the final flux value was the same for P3 and P4. This highlights the sensitivity of the membrane to pressures around the 2 bar area on the limiting pressure.

Variable Flow (Constant Pressure) – Run 28

The final flux value recorded at the highest flow rate (4.74 $m^3 h^{-1}$) was lower than previously measured for other Runs. This could be possibly explained by the sieving effect that occurs when operating at high flow rates, with predominantly smaller droplets being found in the fouling layer, with the larger particles being retained in the bulk liquid. This phenomena was not proved but has been reported by [110] and the effect that the polydispersity has on specific cake resistance in particular although this paper concerned itself with the filtration of colloidal silica particles. Once the fouling layer has been built, the reduction in flow rate has little effect on this layer as the shear forces exerted on it are also becoming less. With no significant drop or readjustment with a decrease in flow rate being different to what was observed with the tubular experiments under Variable flow-constant pressure conditions.

The stability of the emulsion must also be considered due to the variation in oil concentration during Run 28. This could have caused free oil to enter into the membrane pores, thus blocking the use of the pore and resulting in a lower flux. After Run 28, excessive cleaning was undertaken on the membrane to return the PWF to value approaching that measured before the membrane. Cleaning was undertaken for 100 minutes using strong alkaline cleaners, made up from a mixture of sodium hydroxide and dishwasher cleaner.

6 Filtration of Prepared Emulsions

6.1 Emulsion Preparation

This Chapter investigated the filtration of prepared emulsion and the parameters that affect its filterability. For the variable feed concentration experiments, the amount of emulsion required was weighed out and added to the feed tank of the membrane rig whilst the distilled water was being pumped. The rig was operated without a membrane for 30 minutes to allow for the concentrate to be well mixed and temperature stabilised. The experiments were carried out under normal operating conditions.

For the remaining experiments, the emulsion concentration used throughout was 1.5g / litre of oil concentrate to distilled water. The emulsion was prepared by weighing out the required total amount of concentrate and added to two litres of distilled water and mixed rapidly in a vortex blender for five minutes. The resulting mixture was then added to the remaining amount of distilled water in the storage tank of the experimental apparatus and then pumped around the system without a membrane for 30 minutes to stabilise the temperature and to ensure a fully dispersed system..

For the variable conductivity experiments, potassium chloride was used to adjust conductivity. The pure water flux was measured before each experiment and the emulsion was sampled at both the start and end of the experiment for droplet sizing. Permeate analysis was only carried out if it had become cloudy or there was signs of free oil in the feed tank.

6.2 Variable Concentration

The emulsion concentration was varied from 0.75 g / litre to 6 g / litre, with each feed uniquely prepared for every experiment in an identical manner. Table 6.1 summarises the operating conditions for each experimental run and Figure 6.1 shows the specific flux against time for each different concentration, with each experiment carried out under similar operating pressures. Although distilled water was used for each experiment, slight pick-up of conductivity was experienced from previous cleaning runs despite the use of extensive rig and membrane flushing. The density of the emulsion at the varied concentrations varied very slightly and was similar to that of pure water. The viscosity was measured for the 0.75 g / L and 6 g / L concentrations and was very similar to water, therefore a value of 0.873 cSt, the viscosity of pure water at 25 deg C, was used in all calculations.

Each experiment was carried out for 60 minutes with all permeate being returned to the feed tank apart from that collected for inspection and possible analysis. Foaming was experienced throughout each filtration but little visible free oil in or around the system was observed.

6.2.1 Neutral Membrane

Table 6.1 summarises the operating conditions used:

Emulsion Concentration g / litre	PWF $L / m^2 h$ Before	K μScm^{-1}	Pressure bar	Flow m^3h^{-1}
0.75	140	<10	3.46	2.14
1.5	137	<10	3.47	2.07
3.0	128	<10	3.47	2.09
6.0	120	<10	3.47	2.08

Table 6-1 Operating Parameters for Variable concentration experiments using Neutral Membrane.

In all cases, the permeate was clear with oil concentration less than 10 PPM recorded for samples taken for 0.75 g / L and 6 g / L. The final flux values produced at all four concentrations are greater than any fluxes recorded filtering a waste emulsion using the same membrane. The lowest flux value was recorded at the highest concentration as expected but the highest fluxes were obtained at 1.5 g / L. A relatively slow drop in the flux rate was seen for all experiments and the point at which steady state was reached was hard to determine. Table 6.2 summarises Figure 6.1.

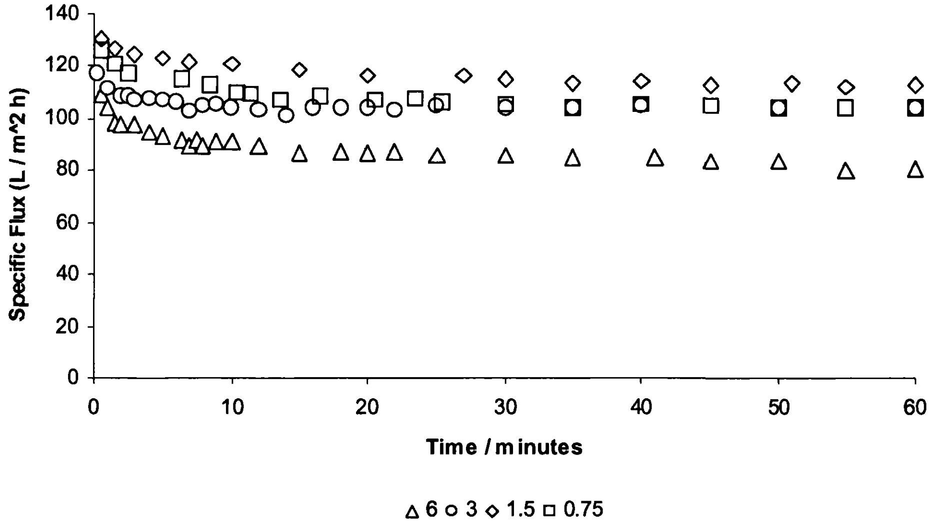


Figure 6-1 Flux Decline during the filtration of a Prepared emulsion using Tubular PVDF Neutral Membrane under Normal conditions – Variable Concentration.

The percentage drop in flux was substantially less than expected when compared to experiments undertaken with waste emulsions, typically 50 – 60 %.

Emulsion Concentration g / litre	J initial L / m^2 h	J final L / m^2 h	% Drop in flux	Final Fouling %
0.75	126	104	18	24
1.5	130	113	13	20
3.0	117	104	11	21
6.0	110	81	24	34

Table 6-2 Summary of Flux Values for Neutral Membrane – Variable Concentration

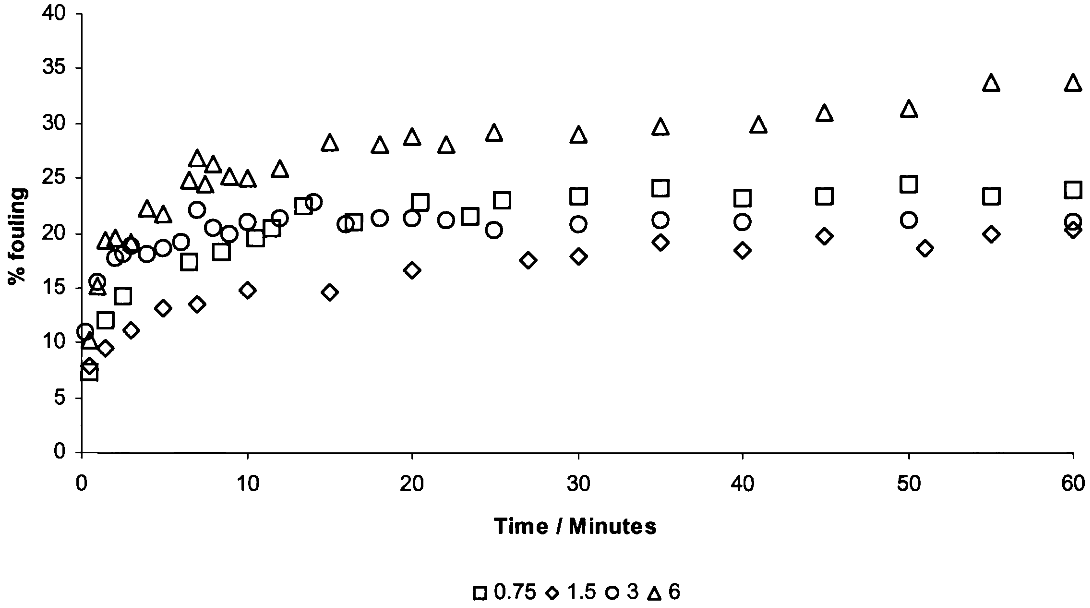


Figure 6-2 Percentage of Total membrane resistance due to fouling – Variable Concentration

The highest rate and percentage of the total membrane resistance caused by fouling was during the 6 g / L experiment which continued to increase with time to a value of 34%. The initial rate of fouling for 3 g / L was next highest although equilibrium was reached after approximately 10 minutes which remained constant for the remainder of the experiment. The lower initial rates were seen for the two lowest concentrations, 0.75 g / L and 1.5 g / L. At 0.75 g / L, equilibrium was reached after 18 minutes with the 1.5 g / L showing a slow but continual rise during the experiment. The lowest value, 20% being recorded for the experiment with the highest flux value, 1.5 g / L, and was approaching that recorded for 3 g / L. The values were substantially less than those calculated using a waste emulsion, typically 60% for the same membrane.

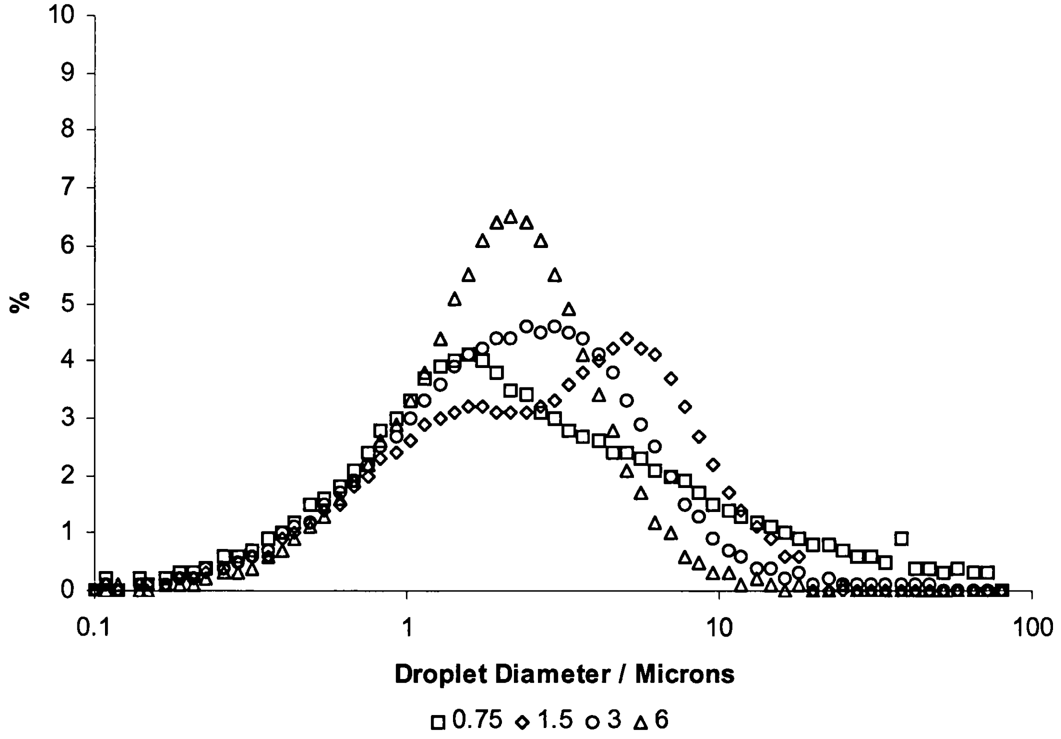


Figure 6-3 Percentage by Volume of Droplet Size distribution for the four concentrations used in Neutral Membrane Variable concentration experiments – Limited Mixing

There was large variation in the droplet size distribution for each concentration. As the concentration was increased, the distribution tends to become narrower with an increase in the percentage of droplets between one and ten microns. This variety in droplet diameter could be due to limited mixing during the experiment and the low amount of energy applied to the system to disperse the concentrate.

There was a slight initial peak at around 1.5 microns for the 0.75 g / L with a gradual decline showing droplets approaching 100 microns in diameter. A smaller number of narrow droplets was seen for 1.5 g / L with a rise in percentage to a peak of around nine microns. A further increase in concentration sees a shift in distribution with a larger number of droplets being measured between one and ten microns. At a concentration of 6 g / L, a narrower distribution was measured with no droplets greater than ten microns.

6.2.2 Anionic Membrane

The experiments were repeated using the Anionic membrane. The following table lists the operating conditions for this set of Runs:

Emulsion Concentration g / litre	PWF $L / m^2 h$ Before	K μScm^{-1}	Pressure bar	Flow m^3h^{-1}
0.75	314	<10	3.47	2.11
1.5	360	<10	3.46	2.09
3.0	336	<10	3.47	2.10
6.0	232	<10	3.47	2.07

Table 6-3 Operating Parameters for Variable concentration experiments using Anionic Membrane.

The conditions used for each run were very similar with only the last run having a lower than normal PWF, suggesting that the membrane had experienced some permanent fouling from the previous experiment. Permeate samples were taken at the two extremes of concentration with values of less than 10 PPM being measured for the oil concentration in each sample.

All the final flux values measured for the Anionic experiments were greater than any flux recorded when filtering a waste emulsion using the same membrane. The flux for the experiments undertaken at 0.75 g / L and 1.5 g / L show an identical slow rate of decline to a steady state of 155 L m^{-2} h^{-1} after 15 minutes. At the higher concentrations, the steady state flux was reached after 3-4 minutes for both experiments. The percentage drop was approaching values expected during the filtration of waste emulsions, these were typically 50 – 60 %. Figure 6.4 is a plot of the flux values against time.

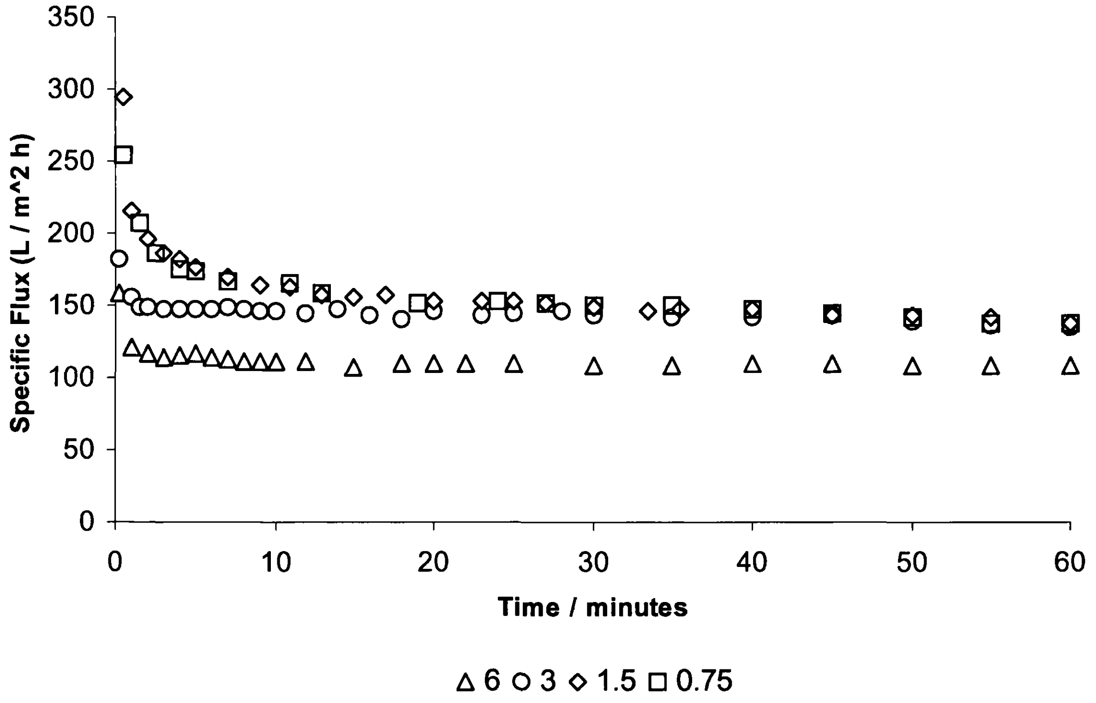


Figure 6-4 Flux Decline during the filtration of a Prepared emulsion using Tubular PVDF Anionic Membrane under Normal conditions – Variable Concentration.

The following table summarises Figure 6.4:

Emulsion Concentration g / litre	J initial L / m^2 h	J steady state L / m^2 h	J final L / m^2 h	% Drop in flux	Final Fouling %
0.75	255	155	137	46	56
1.5	294	155	138	53	63
3.0	181	148	134	26	61
6.0	159	115	108	32	54

Table 6-4 Summary of Flux Values for Anionic Membrane – Variable Concentration

Figure 6.5 shows the percentage of the total membrane resistance due to fouling. These are higher values than those recorded for the neutral membrane but do not reach values recorded using a waste emulsion, typically 85 – 95 %.

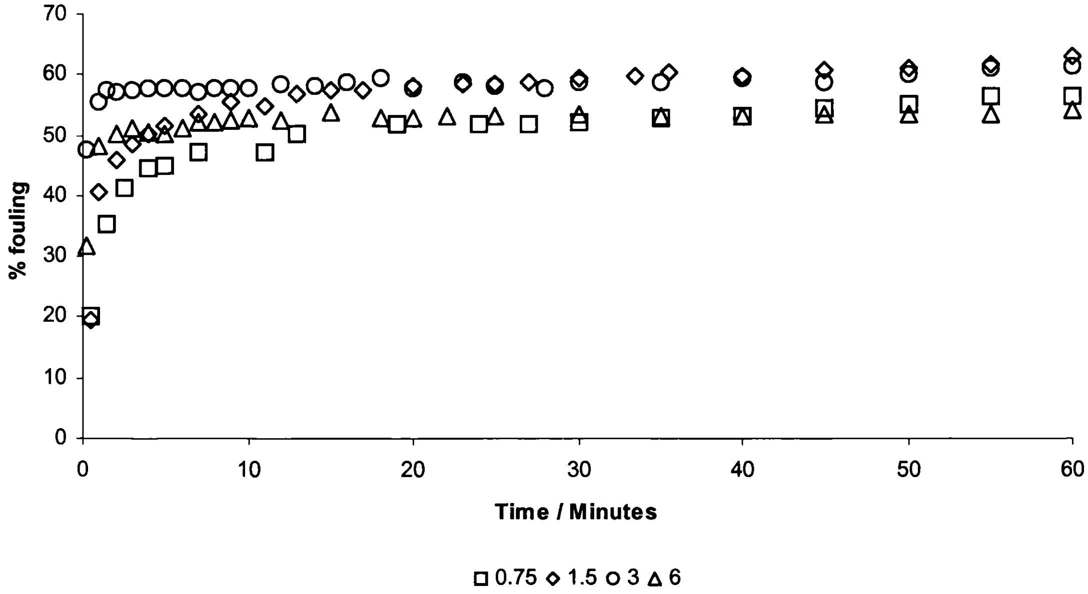


Figure 6-5 Percentage of Total membrane resistance due to fouling for each Experimental run – Variable Concentration

For both 3 and 6 g / L, the initial rate of fouling was high with a steady state being reached very quickly. Despite the lowest final flux, the 6 g / L experiment has the lowest final percentage due to fouling.

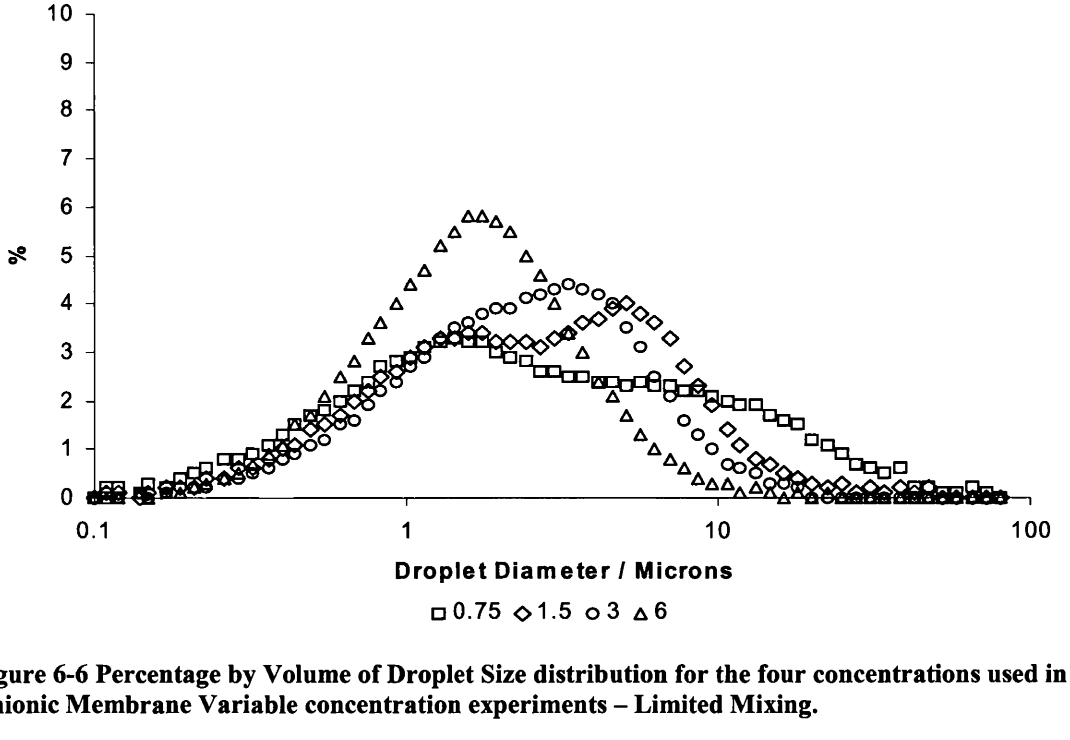


Figure 6-6 Percentage by Volume of Droplet Size distribution for the four concentrations used in Anionic Membrane Variable concentration experiments – Limited Mixing.

The droplet size distribution was similar to that measured for the neutral membrane; this was expected as the same procedure to prepare the emulsion was used for both membranes. The main difference between the figures was that the distribution for the anionic membrane, Figure 6.6, was slightly flatter suggesting that the droplet sizes were over a wider range. At a concentration of 0.75 g / L, there was less of a peak when compared to the neutral results with higher percentages being recorded for droplets in excess of 8 microns in diameter.

6.3 Variable Conductivity

The aim of this part of the work was to draw some conclusions on the effect of conductivity on the filtration of the emulsion. To remove any possible concentration effects, the experiments were conducted using the same concentration, 1.5 g / L and prepared identically. By changing the concentration of potassium chloride in the solution, any electrochemical effects could be qualitatively assessed.

Due to the varied results in droplet diameter in the variable concentration experiments, a vortex mixer was used to create an intermediate emulsion; this was then added to the remaining distilled water being pumped around the system. The potassium chloride was then added whilst the feed was being pumped around for temperature stabilisation. The experiments were undertaken at constant flow and variable pressure. The pressure was increased from the lowest setting to minimise fouling effects for each pressure. A steady state was reached at each pressure setting and the average flux over the last five minutes at each individual pressure was calculated and plotted against the average pressure. During the runs at salt concentration of 0.01 and 0.001 M KCl, permeate was slightly cloudy and it was decided that samples should be taken and analysed.

6.3.1 Neutral Membrane

Table 6.5 summarises the operating conditions for the experiments using the Neutral membrane and Figure 6.7 shows the specific flux against pressure at the various pressure settings and concentration of potassium chloride.

K Cl Conc. Moles / litre	PWF L / m^2 h Before	K μScm^{-1}	pH	Permeate Oil conc. PPM	Pressure bar	Highest flux L / m^2 h	Flow m^{3}h^{-1}
0	112	<10	5.9	3	1.49-4.48	110	2.06
0.1	88	13780	7.2	8	1.49-4.73	116	2.05
0.01	104	1372	6.9	19	1.46-3.86	75	2.03
0.001	90	170	6.9	19	1.37-4.78	87	2.05

Table 6-5 Operating Parameters for Variable Conductivity experiments using Neutral Membrane.

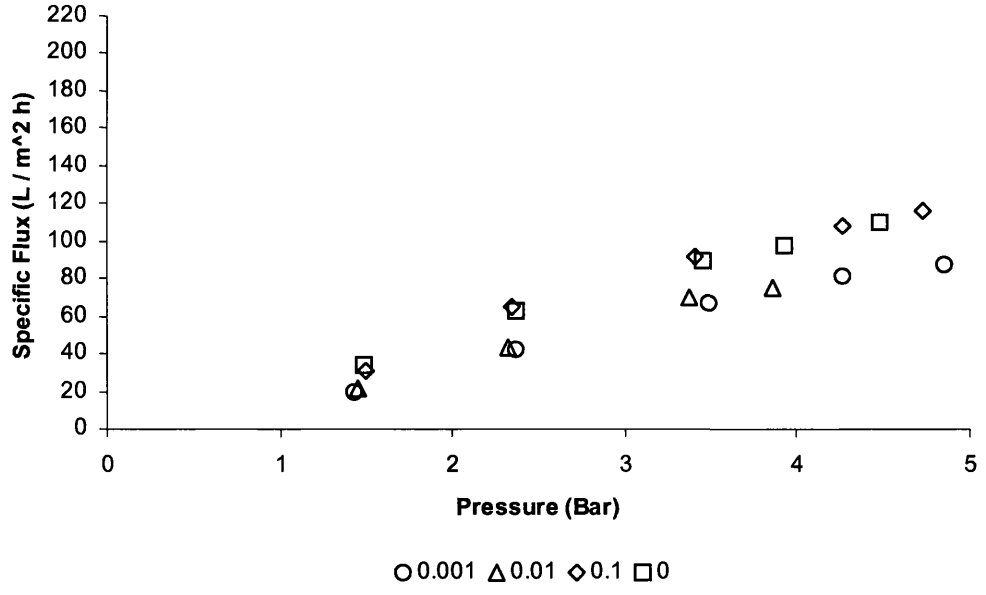


Figure 6-7 Variation in specific flux during the filtration of a Prepared emulsion using Tubular PVDF Neutral Membrane under Variable pressure conditions – Variable Conductivity.

Using the zero conductivity experiment as the base line, it can be seen that at the low concentrations of KCl, there was a negative effect upon the flux. At 0.1 M KCL, the flux pattern was almost identical as the base line. The oil concentration in the permeate was higher than usual in the case of 0.01 and 0.001 M KCl with values measured at the other two concentrations within the expected range of less than 10PPM.

As the pressure was increased, there was no sign of the expected plateau corresponding to the pressure independent region. When compared to experiments under normal operating conditions, i.e. 3.5 bar, the flux values measured are greater than those from waste emulsions, but lower than those measured during the variable concentration experiment at 1.5 g / L. Due to safety reasons, the pressure was not taken to or above 5 bar as there was no data on the maximum operating pressure of the membrane module.

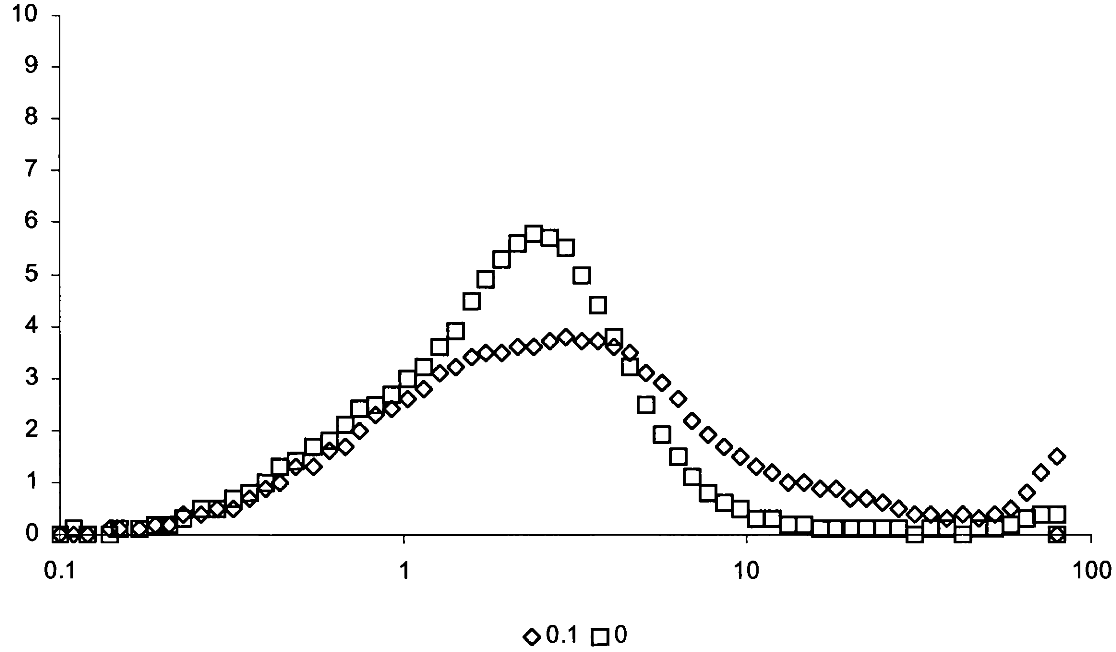


Figure 6-8 Percentage by Volume of Droplet size distribution for 0 and 0.1 M KCl –Neutral Membrane

The only experiment that had an effect on the droplet size was in the case in 0.1 M KCl with the increased conductivity causing a wider droplet distribution with droplets greater than 10 microns and some approaching ninety microns.

6.3.2 Anionic Membrane

The experiments were repeated using the Anionic membrane, the following table summarises the operating conditions used during the experiment.

K Cl Concentration Moles / litre	PWF L / m^2 h Before	K µScm^{-1}	pH	Permeate Oil conc. PPM	Pressure bar	Highest flux L / m^2 h	Flow m^3 h^{-1}
0	274	<10	6.3	10	1.48-4.45	182	2.04
0.1	134	13560	6.9	17	1.48-4.91	205	2.05
0.01	181	1404	6.3	47	1.54-4.34	144	2.05
0.001	136	161	6.9	31	1.38-4.76	148	2.05

Table 6-6 Operating Parameters for Variable Conductivity experiments using Anionic Membrane.

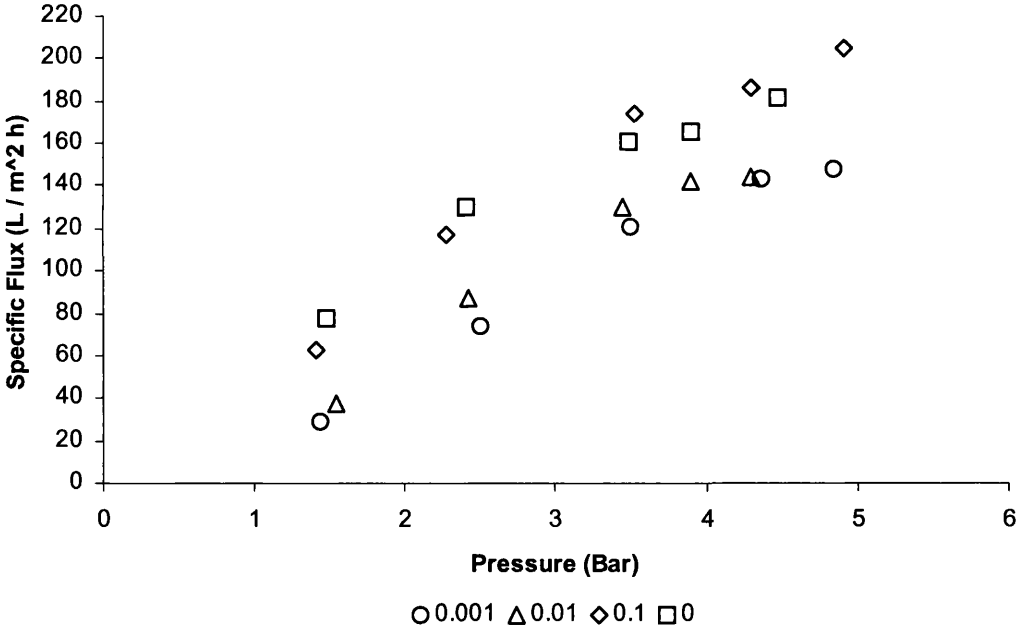


Figure 6-9 Variation in specific flux during the filtration of a Prepared emulsion using Tubular PVDF Anionic Membrane under Variable pressure conditions – Variable Conductivity.

As in the filtration using the neutral membrane, the two lowest fluxes are obtained at 0.01 and 0.001 M KCl. At these conditions, the flux becomes pressure independent at 3.8 bar for 0.01 M KCl and at 4.2 bar for 0.001 M KCl. Although higher flux values were measured for 0 and 0.1 M KCl, the graph shows that these runs are approaching pressure independence at around 4.4 bar.

There was little effect of conductivity on the droplet size except for 0.1 M KCl, the results of which are in Figure 6.10. At the high concentration of KCl, a wider spread of droplet diameters was seen, with similar results to those seen during the Neutral experiments.

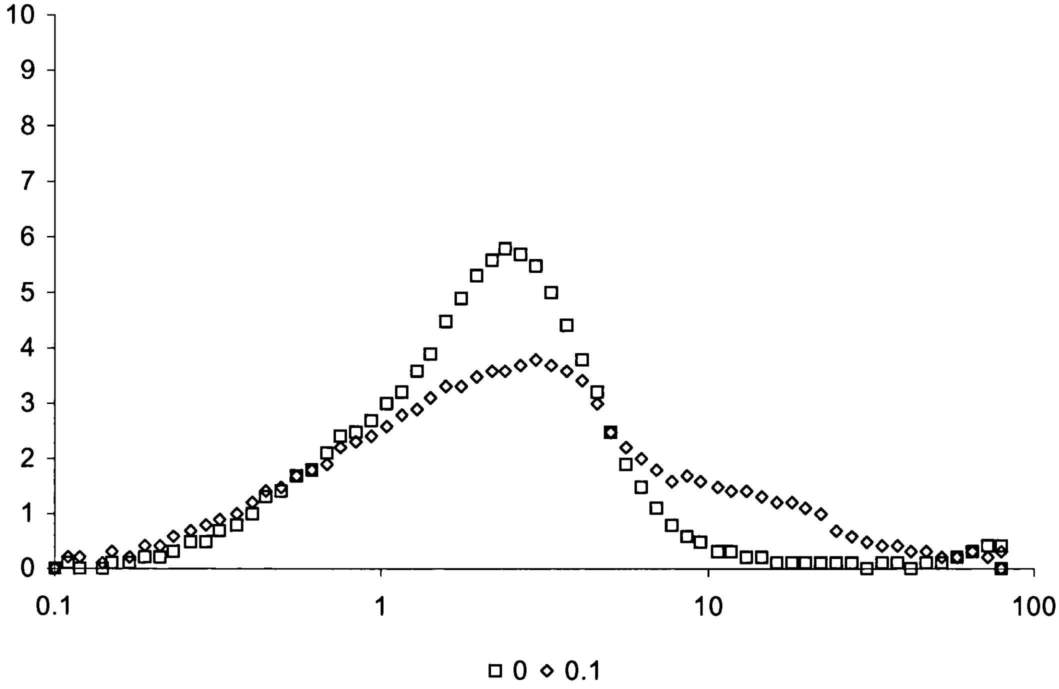


Figure 6-10 Percentage by Volume of Droplet size distribution for 0 and 0.1 M KCl –Anionic Membrane

6.4 *Effect of flow and pressure*

Four experiments for each membrane were undertaken over a range of flow rates, 1 – 4 $m^3 h^{-1}$ using a prepared emulsion of 1.5 g / L and initially mixed with the vortex mixer as described earlier in the Chapter. At each flow rate, the pressure was increased from an initial pressure of 1.5 bar up to around 4 bar within the limitations of the pump. For both membranes at all flows, the permeate produced was consistently clear and was not analysed for oil content.

6.4.1 Neutral Membrane

The operating conditions are detailed in the following table:

Run	Flow rate m^3 / h	Re number	PWF L / m^2 h Before	Pressure bar	Highest flux L / m^2 h
One	1.00	15790	100	1.56-4.38	96
Two	2.06	32690	112	1.49-4.49	110
Three	3.10	49190	96	1.49-4.27	85
Four	4.10	65060	105	1.55-3.70	58

Table 6-7 Operating conditions – Neutral membrane Variable Flow and Pressure.

A steady state was reached at each pressure setting and the average flux over the last five minutes at each individual pressure was calculated and plotted against the average pressure. A graph of specific flux against pressure was plotted in Figure 6.11:

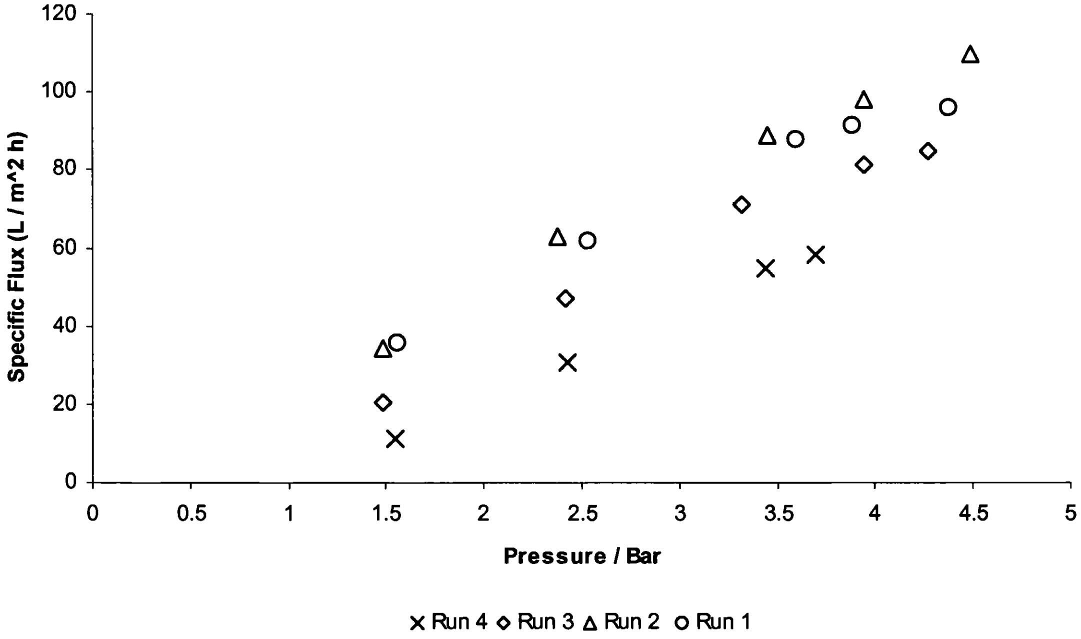


Figure 6-11 Variation of specific flux with pressure at four different flow rates using a prepared emulsion of 1.5 g / L – Neutral Membrane.

At the recommended operating flow of 2 m^3 h^{-1}, the highest fluxes were measured whilst at the highest flows, Run Three and Four, the lowest fluxes were measured. As the pressure was increased, there was no clear cut-off that the experiment was reaching the pressure independent region.

There was little effect on droplet size distribution with the only noticeable difference being measured for Run One. This could be possibly due to the lower flow rate and hence lower mixing allowing some possible coagulation during the experiment.

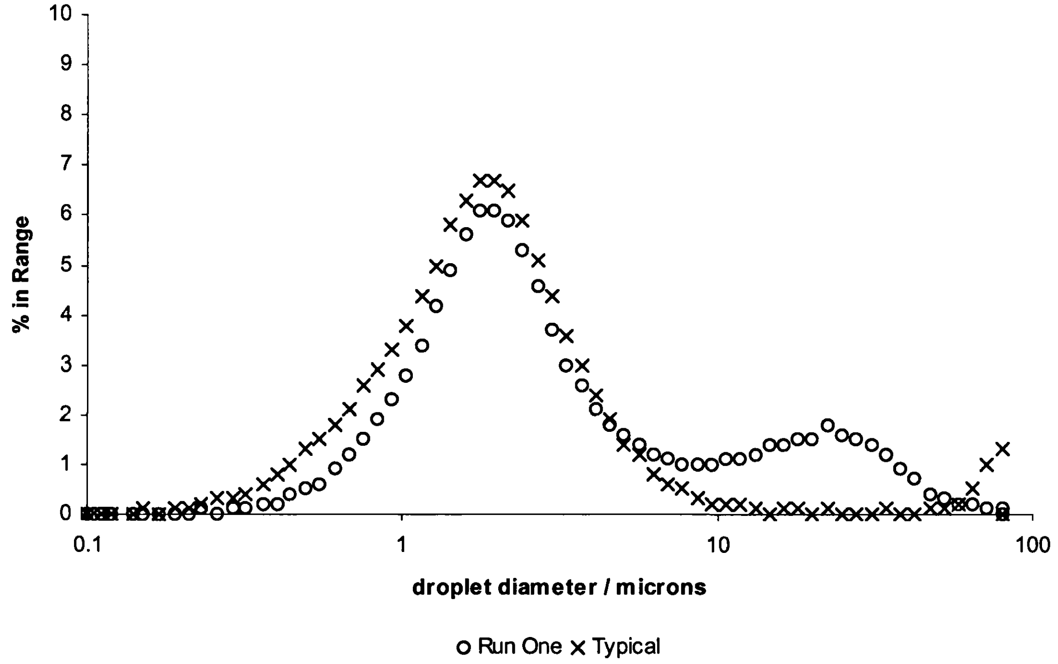


Figure 6-12 Percentage by Volume of Droplet size distribution for Run One and a typical run during variable flow experiments.

6.4.2 Anionic Membrane

The operating conditions are detailed in the following table:

Run	Flow Rate m^3 / h	Re Number	PWF L / m^2 h Before	Pressure bar	Highest flux L / m^2 h
One	1.00	1579	236	1.55-4.43	148
Two	2.04	3237	273	1.48-4.47	183
Three	3.13	4967	216	1.45-4.31	196
Four	4.05	6427	194	1.44-3.74	167

Table 6-8 Operating conditions – Anionic membrane Variable Flow and Pressure.

As before, a steady state was reached at each individual pressure setting and an average of the fluxes calculated over the last five minutes of each pressure setting. A graph of specific flux against pressure was plotted:

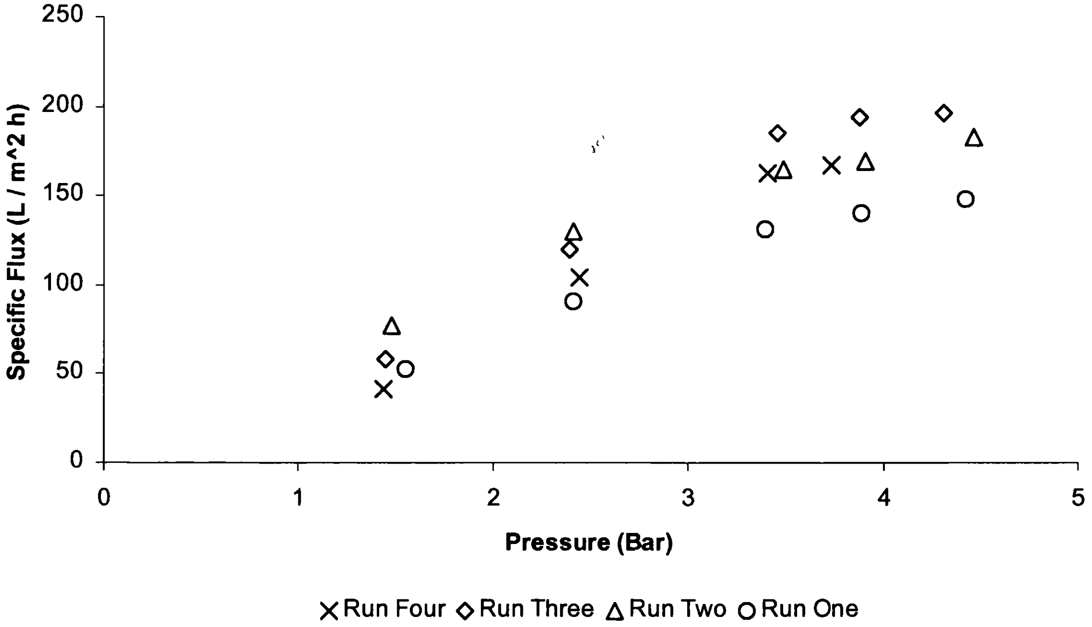


Figure 6-13 Variation of specific flux with pressure at four different flow rates using a prepared emulsion of 1.5 g / L – Anionic Membrane.

Using the anionic membrane, at all flow rates there was evidence that the pressure independent flux region was being approached. The maximum flux was measured at a flow rate of ~ 3 m^3 h^{-1} which was higher than that measured for the neutral membrane. Again, as for the neutral membrane, the highest flow rate produces a very low initial flux at the starting pressure but increases to similar values as for Run Two. At the higher flow rates, Run's Three and Four, the pressure independent region was approached quickest with further pressure increases required for Run's One and Two. There was no effect upon droplet size over the four runs at different flows with the distribution of droplet diameters being similar to the typical distribution presented in Figure 6.12.

6.5 Cleaning

The same cleaning procedures as detailed in Chapter 5.5 were carried out after each experiment. The citric acid rinse produced very little increase in flux with the anionic membrane being affected most. In the case of the Neutral membrane, concentrations of 3 and 6 g / L required more aggressive cleaning measures involving the use of strong alkaline cleaners at elevated temperatures. During these cleaning runs, a brown permeate was produced that was similar to the concentrate used to prepare the emulsions. This was also the case for the anionic membrane using concentrations of 1.5 g / L and above.

6.6 Discussion

6.6.1 Variable Concentration

From the results of the experiments, changes in concentrations of up to 3 g / L of emulsion appear to have little effect upon the final flux values observed, this was in agreement with [92] who filtered in the range of 100-5000 PPM of oil. As only one concentration above 3 g / L was filtered, it was not possible to determine the concentration at which the flux begins to decrease.

Neutral Membrane

Generally, initial flux values for the neutral membrane decreased with an increase in concentration with the final flux values measured for 0.75 g / L to 3 g / L being very similar with only 6 g / L showing any variation. This trend of initial fluxes was expected due to the increased availability of fouling material with an increase in concentration. All final flux values were higher than those measured filtering waste emulsions therefore highlighting the importance of the route that the waste emulsion was moved from the drains and sump to the treatment plant.

In previous experiments with the neutral membrane using a waste emulsion under normal operating conditions, the decline in flux has been generally around 60% of the initial flux values measured. When filtering the prepared emulsion, the maximum flux decline was 24% recorded for the 6 g / L experiment. This suggests that the membrane was fouling quicker as the "steady state" was being reached almost immediately, without the general large flux decline that was typical of the waste emulsion runs. A decrease in PWF was also observed with increasing concentration with additional cleaning steps required after both 3 g / L and 6 g / L experimental runs to achieve a flux approaching the previous PWF.

From Figure 6-3, the droplet distribution for 3 g / L shows an even spread across all the diameters so that a high flux was expected due to the amount of relatively large droplets able to balance out any concentration effects. In the case of 0.75 g / L, the droplets again have a flatter spread with a higher proportion in the range less than 2 microns but with significant droplets being recorded greater than 10 microns. The presence of these smaller droplets potentially being able to form a tighter fouling layer.

In the case of the 6 g / L, the droplet size distribution shows all droplets to be under 11 microns with the majority being around 3 – 4 microns. The shape of the fouling curves for all concentrations was concave-down suggesting that external fouling was the main mechanism of fouling [58]. When compared to the fouling values calculated for the filtration of waste emulsion, at all concentrations of the prepared emulsion fouling values were less.

Anionic Membrane

The initial flux values measured for the four runs generally decreased with a concentration increase. As was the case for the neutral membrane, the final flux values observed at concentrations between 0.75 g / L and 3 g / L are very similar and in the case of the anionic membrane, actually were identical. The highest initial flux was recorded for the 1.5 g / L concentration which also corresponded to the highest initial PWF. The "cleaner" membrane at the start of the 1.5 g / L run, allowing more permeate to pass until the steady state had been reached. The rate of flux decline for the 0.75 g / L and 1.5 g / L experiments was less than for any of the neutral membrane runs suggesting that the membrane was more resistance to the immediate fouling that was seen in the neutral runs and for the anionic membrane at 3 g / L and 6 g / L. The percentage drop in flux from the start was also more typical for the lower concentration experiments with values of 46 and 53 % similar to those measured in the waste filtration.

Final flux values for the prepared emulsion were higher than those recorded during the filtration of an actual waste. This suggesting that the effluent was picking up additional foulants during its route to the sample point. Fouling values are approximately 30% less than those calculated for a waste emulsion using the same membrane. The relatively low values of flux fouling recorded for the 6 g / L experiments can be partly attributed to the low initial PWF. This "restricted" membrane already containing fouling of some sort which after repeated cleaning with both strong and weak alkaline cleaners still producing a low PWF.

During all the experiments, once steady state had been reached for the anionic membrane, the fouling did not continue to increase as was seen in the neutral membrane. The highest fouling percentages being recorded for the 1.5 g / L and 3 g / L, also required additional cleaning and the PWF produced after these two runs lower than the PWF before the 1.5 g / L run.

As in previous experiments using waste emulsions, the anionic membrane produced consistently higher flux values. The anionic membrane also experienced higher a proportion of the percentage of the total membrane resistance due to fouling. Although lower in the experiments using the prepared emulsion, the percentage was high. The inability of the cleaning processes to recover the PWF before the experiments at higher concentrations highlights some concerns with the long term operation at possible higher concentrations of emulsion. Further work needs to be done using the waste emulsion and to look at the levels to which the emulsion can be concentrated up to with a view on minimizing permanent fouling of the membrane. The values suggested by [24] of around 60% oil concentration look very unlikely using the emulsion used from the cold mill of Port Talbot.

6.6.2 Variable Conductivity

No measurements were made of the emulsion droplet or membrane surface charge or zeta potential. The aim of the experiments was to take a qualitative look at the effect of the addition of a known concentration of electrolyte. The addition of an electrolyte should affect the double layer of charge around each droplet as well as having some effect on the membrane surface. By suppressing the charge of the droplet by the addition of an electrolyte, the emulsion droplets are allowed to approach closer to one another. The singularly charged ions of K Cl were not expected to have a large effect on the stabilisation of the emulsion but to suppress surface charges.

At low conductivity runs, 0.01 and 0.001 M K Cl, there was no effect on the droplet diameter but a noticeable rise in oil concentration in the permeate for both membranes. This higher oil concentration measured is approaching levels that would prevent the permeate being reused. At the highest concentration of 0.1 M K Cl, there was evidence that the some coagulation does occur as there was a wider spread of droplet diameters noticeably greater than 8 microns, this was similar for both membranes. The effect of the 0.01 and 0.001 M K Cl on the flux was approximately the same for both membranes, with a 25% difference in fluxes observed between the runs at 0 and 0.1 M K Cl and at 0.01 and 0.001 M K Cl..

It was apparent that conductivity has an effect on the charged anionic membrane and that oil droplets were able to pass through the membrane and enter the permeate. This was less apparent for the neutrally charged membrane.

6.6.3 Variable Flow and Pressure

For the neutral membrane over the range of flow and pressures used during this part of the work, see Figure 6.11, there was no obvious point at which the flux was becoming pressure independent. For Run's One and three, the flux was beginning to tail off with increased pressure suggesting that this region was being approached but due to limitations of the rig and safety, the transmembrane was not increased further. The presence of larger droplets for Run One could have led to a classification situation as the Reynolds number was well into the turbulent region. At a flow rate of 2 m^3 h^{-1}, the pressure at which critical flux could be reached is beyond 4.5 bar. Under the normal conditions using the neutral membrane, the fouling of the membrane, see Figure 6.2, was noticeably less than in experiments filtrating the waste solutions, 77%, see Figure 5.4. This suggests that all previous experiments undertaken using a concentration of 1.5 g / L, have been conducted below this region of critical flux [102] hence the amount of fouling has been minimised.

For the anionic membrane, limiting flux is appearing to be reached for most flow rates and is around 3.5 – 4 bar. When looking at the fouling for all normal runs of the anionic membrane, the percentage of the total membrane resistance due to fouling is much greater than that calculated for the neutral membrane. Values calculated for the "normal" filtration of a waste emulsion using an anionic membrane are 85%, see Figure 5.20, 92% for the filtration of a waste emulsion under variable flow but constant pressure, Figure 5.32. and for the prepared emulsion under "normal" operating conditions, between 55 and 60 %, see Figure 6.5. At the high flow rates, this classification phenomena is amplified, hence that at 3 and 4 $m^3 h^{-1}$, the lowest flux rates under variable pressure were measured.

The fact that the anionic is operating at or very near the pressure corresponding to the critical flux explains the fact that the anionic membrane consistently reports higher percentages due to fouling when compared to similar or identical operating conditions using the neutral membrane. Further work using waste emulsions and variable flow and pressure could be used to determine the range of pressures that corresponds to the point at which critical flux has been reached. By determination of this point, the filtration of the waste emulsions could be optimised to minimise the amount of fouling.

7 Filtration of a Particulate Stream

7.1 Steel Plant Effluent

BOS (Basic Oxygen Steelmaking) Effluent is mainly blow down from gas wash water from the steel making process and local surface drainage. During heavy rain periods, washings from the local drains keep the solids at a relatively constant level. The average concentration of suspended solids is ~ 60 PPM but does vary widely in use. The collected samples were an orangey red in colour that varied in intensity due to variations in feed concentration. For all the filtration runs undertaken on Steel Plant effluent, suspended solids concentrations measured in the permeate were < 4 PPM.

7.2 Sampling and Preparation

The effluent is initially collected in No.5 BOS sump and then pumped to No. 4 effluent sump via a network of pipes, where it can undergo treatment via polymer addition and settling or disposed of to sea. All samples of effluent were collected via a ball valve sample point in 25 litre jerry cans with fifty litres of sample collected each time and transported to the university. As the gas coming off the steel process is very hot, the effluent produced via the gas washing is warm, ~ 20 ^{o}C. An experimental operating temperature of 25 ^{o}C was deemed suitable to allow for any possible variations in seasonal temperatures and had been consistently maintained via the current rig cooling during previous experiments on emulsions. No preparation of the samples was carried out.

7.3 Analysis and Characterisation of Particulates

The effluent sample was introduced into the feed tank and the solution pumped around the system with no membrane in place allowing the experimental pressure and flow to be pre-set as described in Chapter 4.3.2. A 500ml sample was then removed from the feed tank in a glass sample jar and taken to the works to be analysed via the Chemical Services lab. The basic analysis consisted of pH, conductivity, oil concentration, suspended solids and any further analysis specified for the identification of particle material.

Two major metal constituents of the effluent were iron and zinc, on average 22% and 11% by weight respectively with trace elements of chromium and lead. The metal content analysis was done using ICP AES as detailed in Chapter Four. Another sample was also taken for the sizing experiments which due to the dilute nature of certain samples requiring greater volumes within the Malvern Mastersizer to produce reliable results.

7.4 Filtration Runs

Only one membrane was used to filter the particulate waste stream due to the time limitations placed on the project. This was a Polysulphone hollow fibre membrane supplied by Koch and detailed earlier in chapter Four. The recommended operating pressure from Koch was 2 bar and a flow rate of 4 $m^3 h^{-1}$. For the experimental runs, three different flow ranges were selected that covered the transition from laminar to turbulent flow within the membrane fibres.

Permeate sampling was undertaken as described in Chapter 4 and during the experimental runs, 25 litres of permeate was collected after 45 minutes of operation. In general, during the filtration of the different feeds, the solution in the feed tank would become clearer during the experimental run.

Table 7.1 summarises the general operating conditions for the experimental runs:

Flow range	Actual flow $m^3 h^{-1}$	Trans membrane bar	Reynolds Number	ss. conc mg / L	flux start $L / m^2 h$	flux finish $L / m^2 h$	% drop	pH	K μScm^{-1}
2 $m^3 h^{-1}$									
Run One	2.15	1.86	1244	21	210	150	28.6	7.6	493
Run Two	2.19	1.93	1270	27	197	147	25.4	7.7	464
Run Three	2.04	1.85	1180	21	185	144	22.2	8.3	437
Run Four	2.1	2.10	1241	70	226	157	30.5	8	474
Run Five	2.04	2.04	1180	7	176	142	19.3	7.6	442
3 $m^3 h^{-1}$									
Run Six	3.08	1.96	1780	49	205	160	22.0	7.9	467
Run Seven	3.16	1.87	1830	54	199	149	25.1	7.3	484
Run Eight	3.11	1.98	1800	39	198	141	28.8	7.8	459
4 $m^3 h^{-1}$									
Run Nine	4.16	1.88	2406	122	231	153	33.8	8.3	531
Run Ten	4.08	1.89	2360	36	191	140	26.7	7.7	434

Table 7-1 All flow summary of particulate filtration experiments

7.4.1 Flow range 2 $m^3 h^{-1}$

Five experiments were undertaken at this flow range. The following Figure, 7.1, is the specific flux graph against time for Run's 1 to 3. These runs had very similar suspended solids concentrations with only slight variations in operating conditions for the three runs and produced very similar results. For Run's 1, 2 and 3, 25 litres of permeate were collected during the final ~15 minutes of the experiment. This effectively doubled the concentration in feed suspended solids.

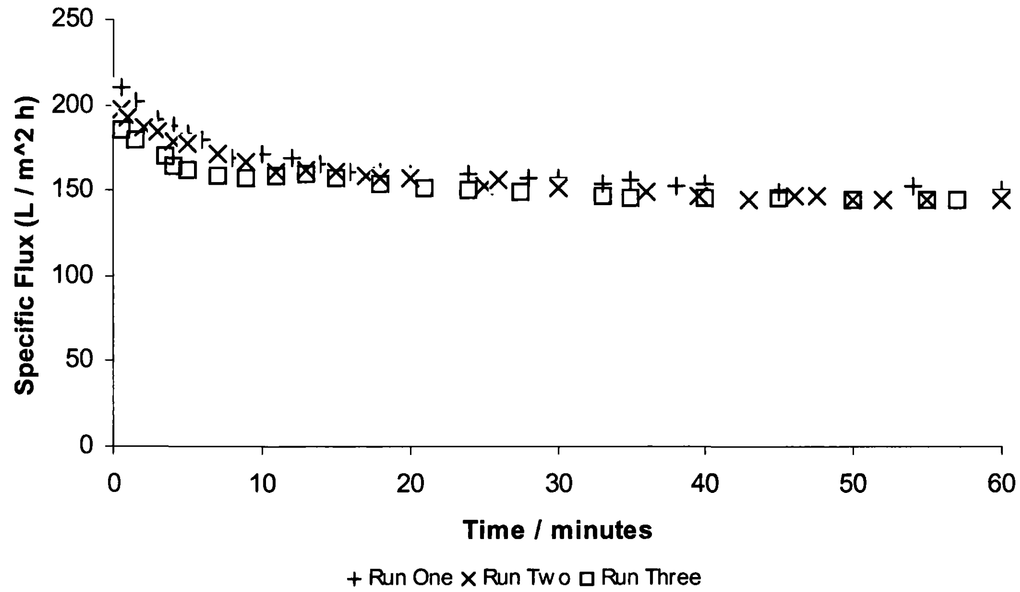


Figure 7-1 Flux Decline during the filtration of steel plant effluent using a PS hollow fibre module with a flow range of 2 m^3 h^{-1} and ~ 2 bar – Runs 1 to 3

Table 7.2 summarises Figure 7.1:

Run Number	Actual flow m^3 h^{-1}	Trans membrane bar	Re Number	ss. conc mg / L	flux start L / m^2 h	flux Steady-state L / m^2 h	time to Steady-state minutes	flux finish L / m^2 h	% drop
Run One	2.15	1.86	1244	21	210	158	9	150	28.6
Run Two	2.19	1.93	1270	27	197	156	9	147	25.4
Run Three	2.04	1.85	1180	21	185	157	9	144	22.2

Table 7-2 Summary of Runs One to Three undertaken at ~ 2 m^3 h^{-1}

Very similar final flux values were measured for each run with the decline in initial flux being almost identical with just the offset from the difference in initial flux values accounting for the different starting point. As the filtration run continued, the specific flux gradually decreased. Permeate collection began after ~ 45 minutes of operation and had only a slight effect on specific flux.

Particle size analysis was undertaken using the Malvern Mastersizer, see Figure 7.2:

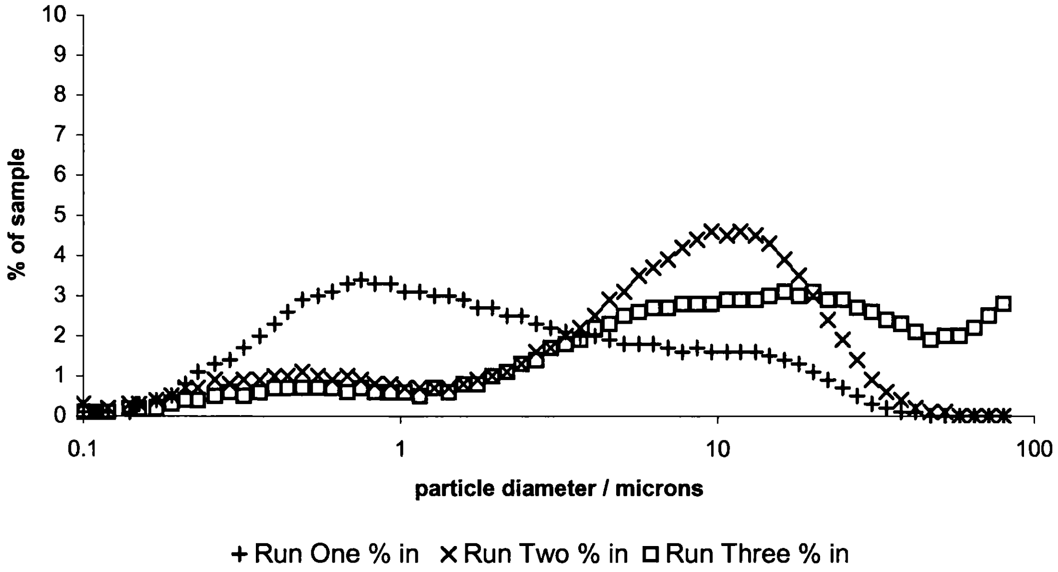


Figure 7-2 Percentage by Volume of Particle distribution for Run's One to Three at ~ 2 m^3 h^{-1}

There was a large variation in the particle diameter for each of the runs. Run 1 has a widely distributed particle diameter with 50% by volume of particles under 1.5 microns, for run two, 50% of the particles were under 7 microns and for run three, 50% of the particles were under 5.5 microns. The effect of particle size can be seen upon the fouling percentage of the membrane.

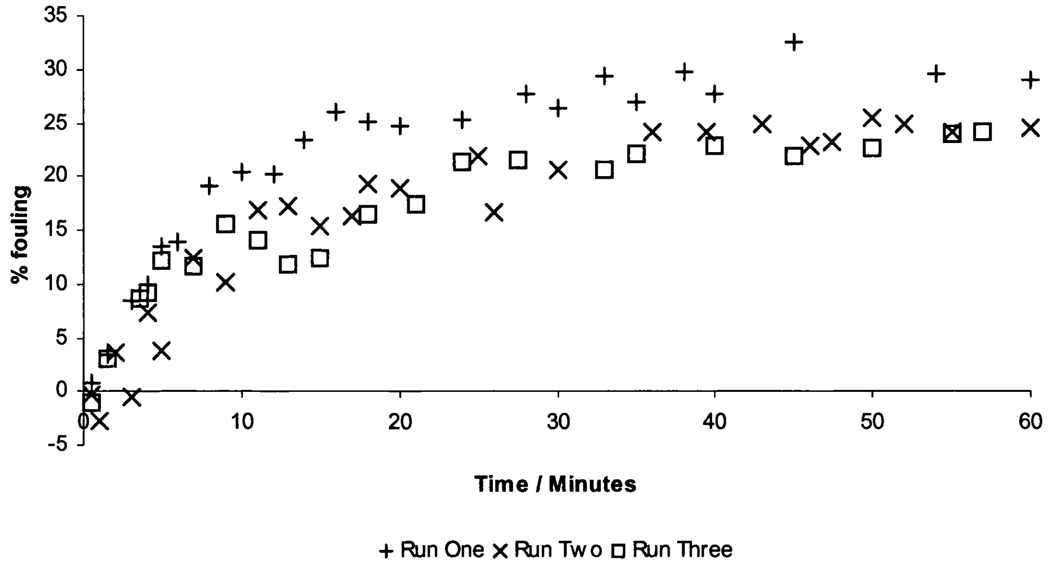


Figure 7-3 Percentage of Total membrane resistance due to fouling – Runs 1 to 3

Initial fouling rates are similar and it was after ten minutes that the differences became more apparent. Run 1 has the highest number of particles under 1.5 microns and this was reflected in the highest percentage due to fouling. For Runs 2 and 3 the 50% cut off for particle diameters are in similar regions with Run 3 having slightly larger particle diameters and less fouling. Due to the low Reynolds number in each fibre, the time taken for classification effects due to different diameters was longer than for turbulent systems.

Runs 4 and 5 had a large difference in feed concentration of particulates with Figure 7.4 showing a graph of specific flux against time. The initial flux measured for the higher concentration of solids in Run 4, produced a higher initial flux of 226 L m^{-2} h^{-1} and more rapid decline in flux than previous experiments. A steady state flux value for Run 4 was the same as in previous runs, 158 L m^{-2} h^{-1} with no further drop in specific flux during the remainder of the experiment. Run 5, despite the lower feed concentration, had a lower initial flux and flux declined throughout the experiment with steady state reached after 30 minutes.

25 litres of permeate was collected after 45 minutes of the experimental runs which corresponded to a slight decrease in flux for Run 5, the lower concentration feed, but no effect on Run 4 flux. Similarly, an increase in fouling was observed for Run 5 but not for Run 4. The PWF measured before Run 5 was low at 178 L m^{-2} h^{-1} due to problems cleaning the membrane after Run 2 at 4 m^3 h^{-1}.

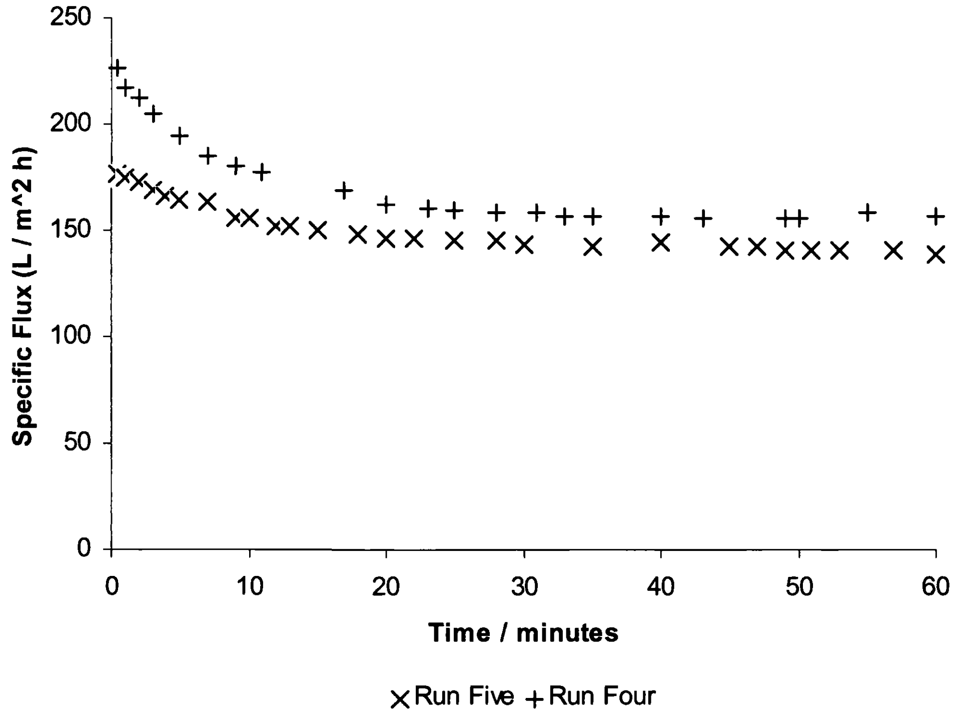


Figure 7-4 Flux Decline during the filtration of steel plant effluent using a PS hollow fibre module with a flow range of 2 m^3 h^{-1} and ~ 2 bar – Runs 4 and 5

The following Table summarises Figure 7.4:

Run	Reynolds Number	ss. conc mg / L	flux start L / m^2 h	flux Steady -state L / m^2 h	Time to Steady -state Minutes	flux finish L / m^2 h	% drop	pH	K µScm^{-1}
Run 4	1241	70	226	158	23	157	30.0	8	474
Run 5	1180	7	176	157	30	142	19.3	7.6	442

Table 7-3 Summary of Runs 4 and 5 undertaken at ~ 2 m^3 h^{-1}

Due to the dilute nature of the particulates in Run 5, it was not possible to measure the particle diameter using a Mastersizer. For Run four, the 50% cut-off of particle diameters was 6 microns which was similar to Runs 2 and 3. The final fouling percentage for Run 4 was greater than previous runs, 36%, and this was possibly caused by the higher concentration in the feed. For Run 5 the final fouling percentage was 24%.

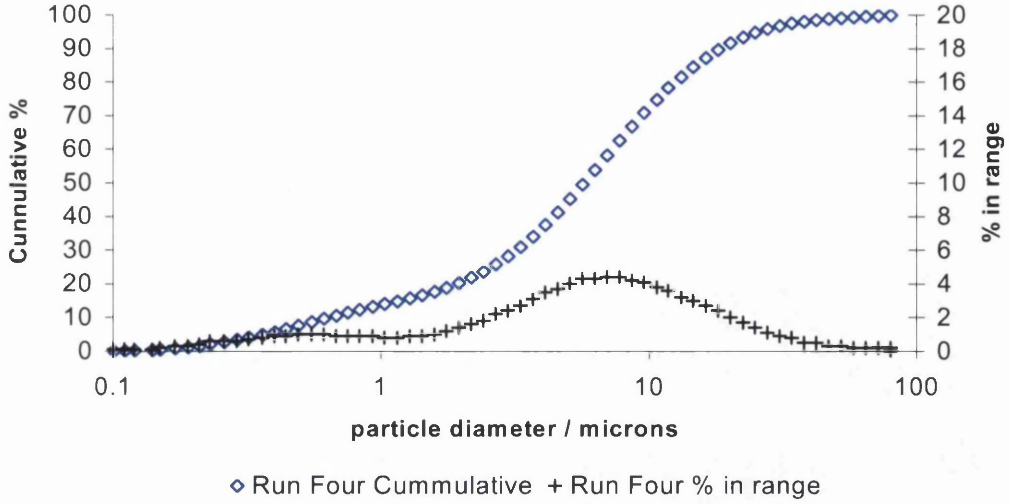


Figure 7-5 Percentage by Volume of Particle size distribution for Run Four

The low fouling percentage of Run 5 was expected due to the lower concentration than Run 4 as the amount of potential fouling material is less but is not as widely different as expected. The inability to measure the particle size makes it impossible to speculate on the presence of smaller diameter particles thus producing a tighter and more resistant fouling layer.

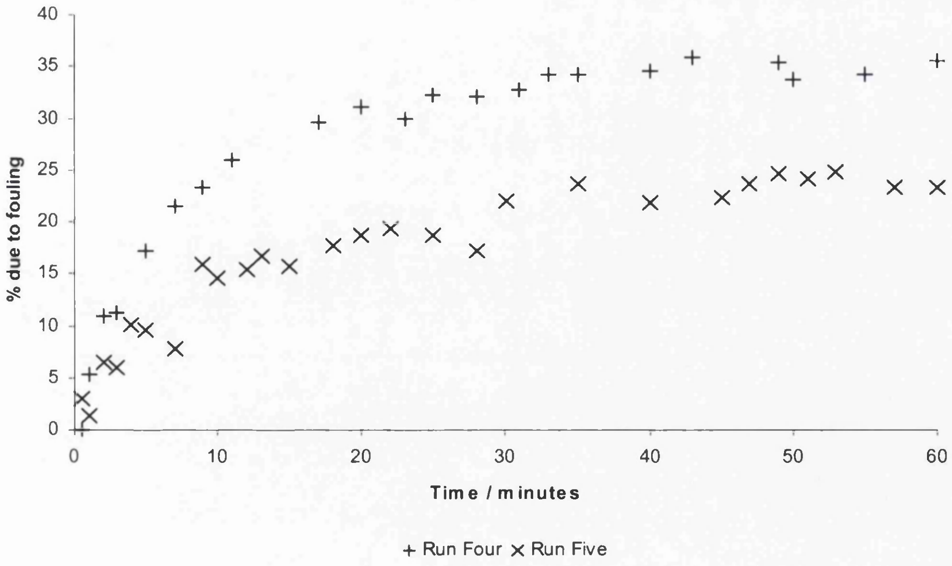


Figure 7-6 Percentage of Total membrane resistance due to fouling – Runs 4 and 5

7.4.2 Flow range 3 $m^3 h^{-1}$ (Runs 6 -8)

Three experiments were undertaken at 3 $m^3 h^{-1}$ and operating pressure of 2 bar., each lasted for 60. As the feed flow rate has been increased, the Reynolds number has also increased to the transition region between laminar and turbulent flow. The final flux values and percentage drop in flux yield very similar results to the experiments carried out at the lower flow of 2 $m^3 h^{-1}$. For all the runs, approximately 25 litres of permeate was collected after 45 minutes of filtration.

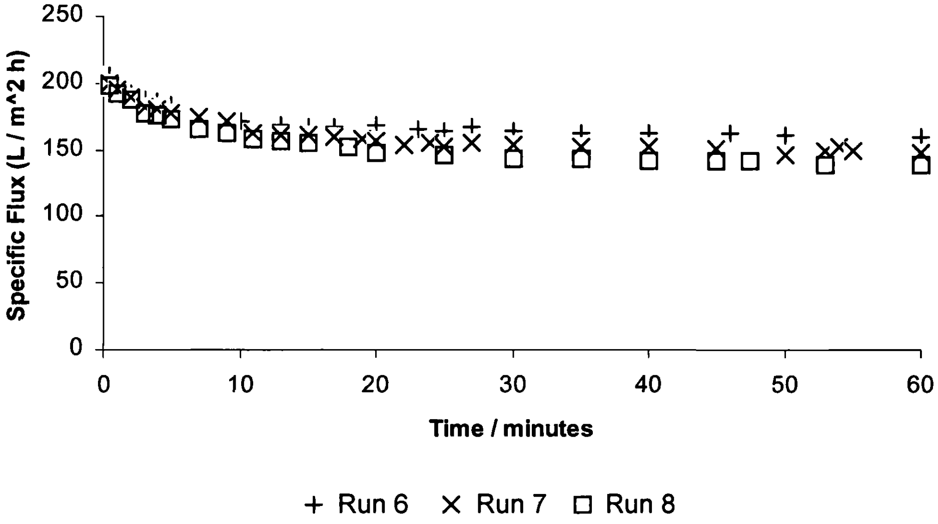


Figure 7-7 Flux Decline during the filtration of steel plant effluent using a PS hollow fibre module with a flow range of 3 $m^3 h^{-1}$ and ~ 2 bar – Runs 6 to 8.

The following Table, Table 7.4, summarises Figure 7.7:

Run	Reynolds Number	ss. conc mg / L	flux start L / m^2 h	flux Steady state L / m^2 h	Time to Steady State minutes	flux finish L / m^2 h	% drop	pH	K µScm^{-1}
Run 6	1780	49	205	168	15	160	22.0	7.9	467
Run 7	1830	54	199	157	20	149	25.1	7.3	484
Run 8	1800	39	198	148	20	141	28.8	7.8	459

Table 7-4 Summary of Runs 6 to 8 undertaken at ~ 3 $m^3 h^{-1}$

At this higher flow, there was a higher degree of separation between the final fluxes for each run that was not seen in the lower flow experiments. The particle distribution for the three runs was similar below one micron but Run 7 has a higher number of particles below ten micron. The 50% cut off for Run 6 was 5.5 microns, for Run 7 was 4.5 microns and for Run 8 was 7.75 microns.

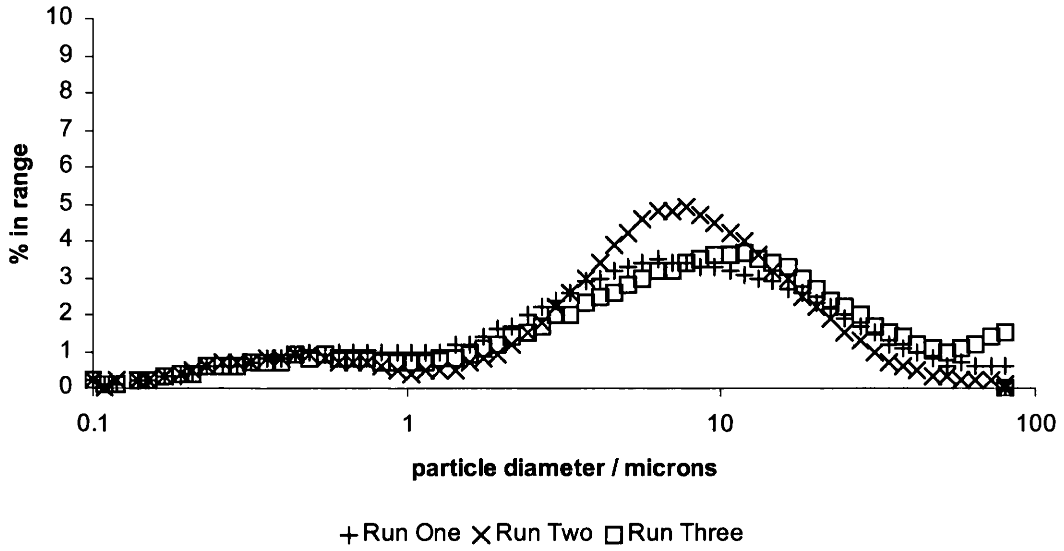


Figure 7-8 Percentage by Volume of Particle distribution for Run's One to Three at ~ 3 m^3 h^{-1}

Very similar initial rates of fouling were seen for all three runs, Figure 7.9, with the highest percentage from fouling being 33% for Run 8. For Run's 7 and 8, the percentage fouling continued to increase with time whereas for Run 6 only a slight increase in fouling was seen by the end of the experiment. At the end of Run 6, the fouling percentage was 24% and for Run 7 was 27%. The further flux decline from the steady state to final measured flux was expected due to the concentration of the solution by removing the permeate after 45 minutes of operation.

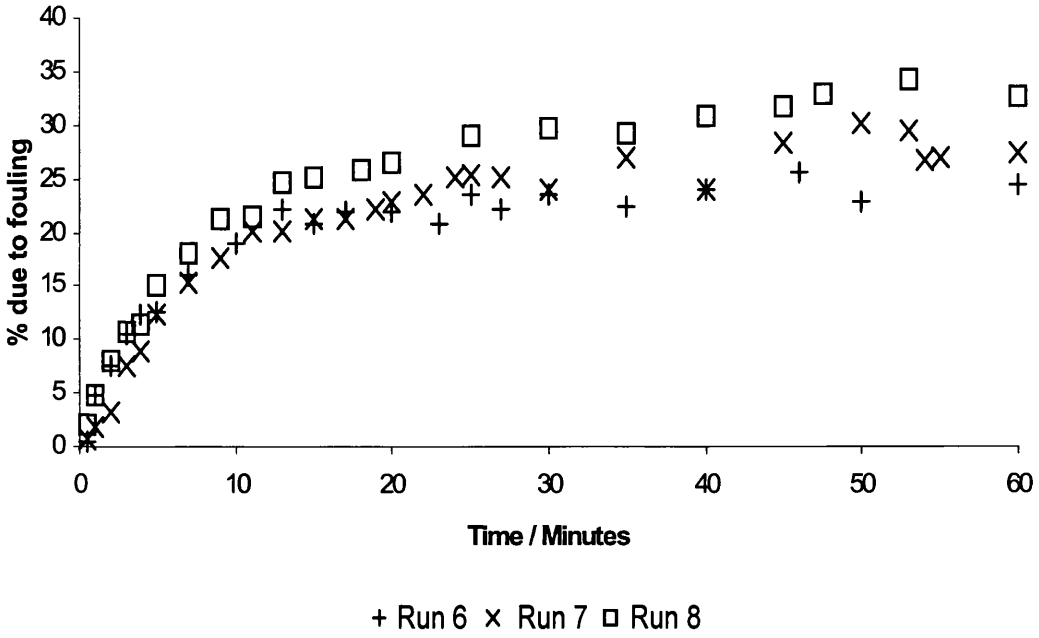


Figure 7-9 Percentage of Total membrane resistance due to fouling – Runs 6 to 8 at ~ 3 m^3 h^{-1}

7.4.3 Flow range 4 m^3 h^{-1} (Runs 9 -10)

Two experiments were carried out at the membrane manufactures recommended flow rate of 4 m^3 h^{-1} and a pressure of ~2 bar and the runs lasted 60 minutes. There was a large difference in concentration of the suspended solids in the feeds, 122 PPM compared to 36 PPM. Approximately 25 litres of permeate was collected for both runs during approximately the last 15 minutes of the experimental run. In the case of Run 10, the feed remained slightly cloudy throughout the experiment.

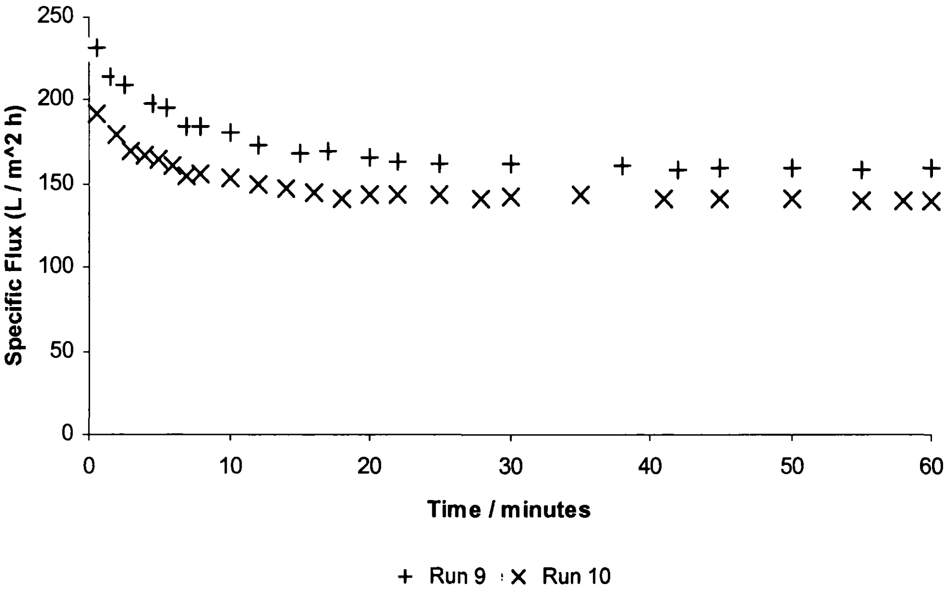


Figure 7-10 Flux Decline during the filtration of steel plant effluent using a PS hollow fibre module with a flow range of 4 m^3 h^{-1} and ~ 2 bar – Runs 9 and 10.

The following Table, Table 7.5 summarises Figure 7.10:

Run	Reynolds Number	ss. conc mg / L	flux start L / m^2 h	flux Steady -state L / m^2 h	Time to Steady -state Minutes	flux finish L / m^2 h	% drop	pH	K μScm^{-1}
Run 9	2406	122	231	163	22	153	33.8	8.3	531
Run 10	2360	36	191	141	18	140	26.7	7.7	434

Table 7-5 Summary of Runs 9 and 10 undertaken at ~ 4 m^3 h^{-1}

At the higher feed concentration, the greater percentage drop in initial flux was observed after 60 minutes. The time to reach steady state was slightly longer for Run 9 than Run 10 with only a slight further decrease in flux for the second run. After steady state had been reached for Run 9, the flux continued to drop off for the remainder of the experiment.

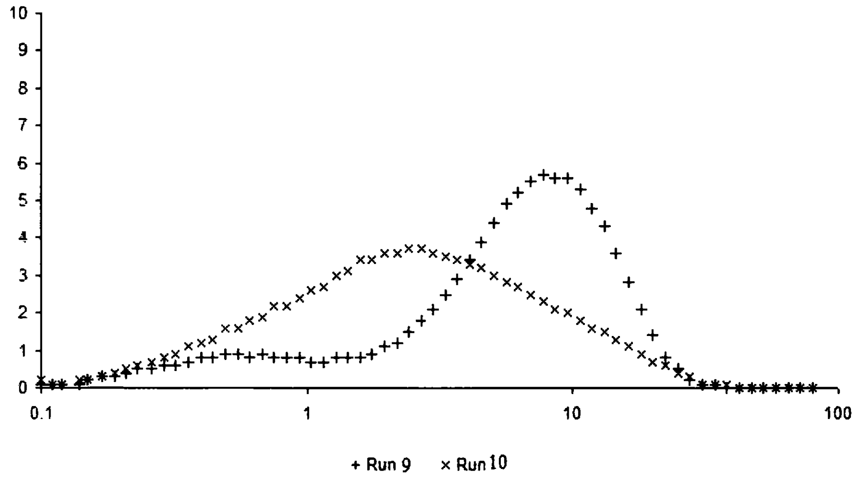


Figure 7-11 Percentage by Volume of Particle distribution for Run's 9 and 10 at ~ 4 m^3 h^{-1}

The particle diameter for Run 9 had a 50% cut-off at 6 microns and for Run 10, 2.4 microns. A much wider spread of particle diameters is seen for Run 10 with ~12% of particles being under 1 micron for Run 9.

For Run 9, the initial flux was greater than the PWF measured before the experiment and this consequently resulted in the percentage of the total membrane resistance due to fouling to initially be negative over the first 1.5 minutes, see Figure 7-12. As the experiment progresses, the fouling increases at a slow rate with similar values being calculated for both runs despite the difference in feed concentration of suspended solids. The higher concentration of Run 9 has a slightly greater fouling percentage compared to Run 10, of 28% and 23% respectively. Run 9 shows no change in fouling after 45 minutes with Run 10 showing only a slight increase in fouling after this time.

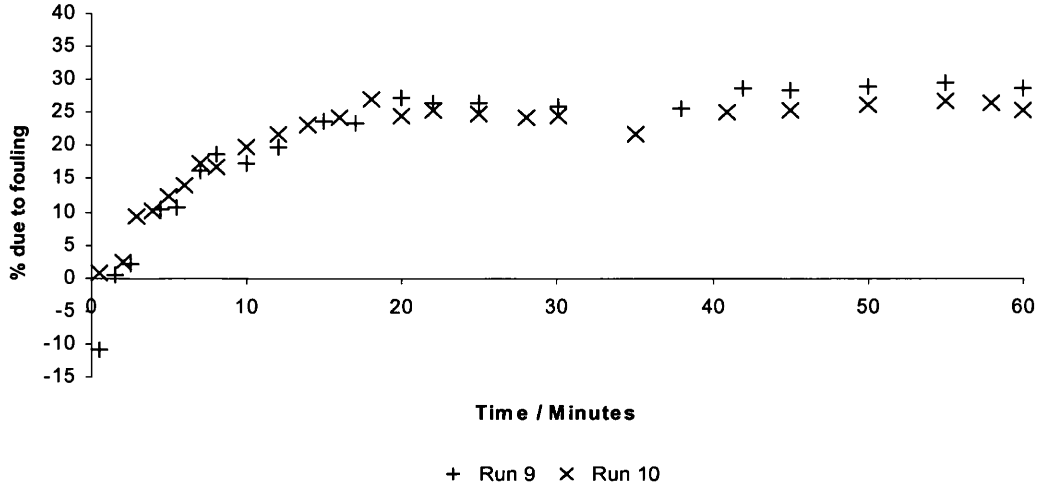


Figure 7-12 Percentage of Total membrane resistance due to fouling – Runs 9 and 10

7.5 Membrane Cleaning

The membrane was benchmarked before each experimental run using double distilled water to calculate the resistance of the clean membrane. This was under taken at ~2 bar pressure and at the flow rate that the experiment was to be operated at i.e. if the run was what at ~ $2m^3 h^{-1}$, then the PWF was measured at using this flow rate.

Over the duration of all the particulate filtration experiments, the PWF of the clean membrane only varied slightly for each individual run. The PWF before each experiment except Run 2 was between 190 and 195 L $m^2 h^{-1}$ with the first PWF undertaken for the membrane before use measured at 210 L $m^2 h^{-1}$ and before Run 5 at 2 $m^3 h^{-1}$. Further cleaning after this run was able to recover a PWF in the expected range. The fact that the PWF was recoverable each time suggests that the amount of permanent fouling, if any, was negligible. A PWF of 195 L $m^2 h^{-1}$ typically corresponds to a membrane resistance of $3.88 \times 10^{12} m^{-1}$.

The basic membrane cleaning procedure after each run was generally the same. After the experiment had ended, the feed tank would be drained and the rig cleaned as detailed in Chapter 4.3.4 Rig Cleaning. Once the rig was fully drained, 30 litres of double distilled was added to the feed tank and this was used to flush the membrane module. To do this, the permeate off take from the membrane was shut to prevent any transmembrane pressure force and the distilled water circulated around the system at a low flow and pressure, typically this was 0.8 bar and 1 $m^3 h^{-1}$.

The pump was started and ~4 litres of the feed was collected immediately after the discharge pipe back into the feed tank to prevent any contamination of the feed solution. The initial flushes were dark in colour and contained high concentrations of particulates. For each further flush, the solution would become progressively clearer with flushing undertaken until the solution ran clear. Once clear, the feed tank would be topped up to contain approximately 25 litres of distilled water and 1.5 g / L of alkaline dishwasher cleaner was then added.

This alkaline solution, pH ~ 10, was circulated around the system for 10 minutes under the low flow and pressure settings with the permeate valve still shut off. The initial temperature was approximately 25 °C but there was no attempt to maintain a steady temperature during cleaning although the temperature would only increase by a 2 – 3 degrees during this process. On some occasions, the cleaning solution would turn a dull red in colour as any fouling material on the membrane on in the system was dissolved by the alkaline solution.

The PWF was then measured after the initial alkaline cleaning stage to determine the effectiveness of the cleaning. On some occasions no further cleaning was required, i.e. if the PWF was ~ 190 L m^2 h^{-1}, if this was not the case, then further alkaline cleaning was undertaken using a 0.4 wt% Na OH solution. The feed tank contained 25 litres of distilled water and a separate solution containing the weight required of Na OH was made up using some of the water from the feed tank and solid Na OH pellets, supplied from Fisher Scientific, Uk. Once all the Na OH had dissolved it would then be added to the feed tank and circulated through the system at ~0.8 bar but at a flow rate of ~2m^3 h^{-1} for 15 minutes.

The permeate valve would initially be shut off for the first ten minutes but then opened for the last five to allow the cleaning solution to permeate the membrane. The rig was then drained and rinsed thoroughly to remove any traces of Na OH using distilled water. The permeate valve was shut during this operation. Once rinsed, the PWF was then measured for the membrane and compared to the range of 190 - 195 L m^2 h^{-1} if the PWF was not within this range, the Na OH rinse would be repeated at a temperature of ~35°C. The PWF measured before Run 5 at 2 m^3 h^{-1} was below this but due to time constraints, the Na OH rinse was repeated once only and the PWF measured and used for the following experiment.

In general, the amount of cleaning required after an experimental depended on the experiments operating flow rate. At the higher flow rates, the membrane was more difficult to clean and required the use of an extra Na OH rinse. This is believed to be because at the higher flow rates, the smaller particles, i.e. those less than one micron are preferentially deposited on the membrane surface due to sieving effects, authors [98] and [99] confirming that this is the case for polydisperse solutions. No work could be found in the literature that reported on the effect of filtration flow rate on cleaning requirements. The ability to successfully operate a full-scale plant at maximum efficiency of both membrane and operating costs, in particular hydraulic energy for pumping and cleaning chemical usage depends on the control of membrane fouling.

7.6 Discussion

A wide variation in the feed concentration of suspended solids has been filtered using an actual membrane module available for larger scale commercial plants. The effect of feed flow rate on the flux rate has been investigated with the percentage of the total membrane resistance during filtration due to fouling calculated. Particle size distribution has also been measured for all except one feed, this was due to the dilute nature of the feed in question, in all cases, a polydisperse feed solution was used. A general comment on cleaning has also been made and a broad assessment of the ability to recover the PWF before each experimental run, i.e. the amount of permanent fouling that has occurred due to the filtration of the effluent.

The quality of permeate produced during the experimental runs was consistently excellent, with suspended solids less than 4 mg / L for all runs. This was due to the MWCO of the membrane, 50 000 and its corresponding tight pore size. With the small pore diameter used and the low percentage of the total membrane resistance during the filtration being caused by fouling, less than ~36% in all cases, the major fouling mechanism was not thought to be due to any pore blocking or plugging.

During the filtration of the effluents, the solution within the feed tank became progressively clear; a phenomenon also reported by [112] during the filtration of polystyrene latex particles, this is due to the effect of particle adhesion to the pilot plant and membrane surfaces. This was proved to some extent by the flushing of the membrane after each experiment producing a discoloured solution containing a high concentration of solids as well as visually during the runs although the amount of particle deposition on the feed tank surface was minimal.

The conductivity and pH of the feed varied only slightly over the range of experiments, 437 – 531 microsiemens and pH ranging from 7.3 – 8.3. Many authors have reported on the effect of these parameters on membrane and particle surface charge and the influence upon these on filtration rates, a thorough review given in [101]. This study acknowledges the importance of these factors but is unable to make any comments based on the experimental work presented in this chapter. In the context of the theme, the addition of chemicals to alter either pH and / or conductivity to enhance membrane filtration will have an effect on the operating costs of the process and may possibly render the permeate unsuitable for further reuse due to a change in either of these parameters.

For all experimental runs the starting feed volume was reduced by half via the removal of permeate from the system. There was little or no effect on the flux rate of the membrane during this concentration step with some effect, normally an initial increase in fouling of 3 –4 % which then returned to levels observed before the removal of permeate. No data on the effect of concentrating a dilute feed from a steel plant effluent was found in the literature. The ability of the membrane to concentrate the feed whilst maintaining a high flux will increase the usable water recovery whilst prolonging the operation of the plant between cleans.

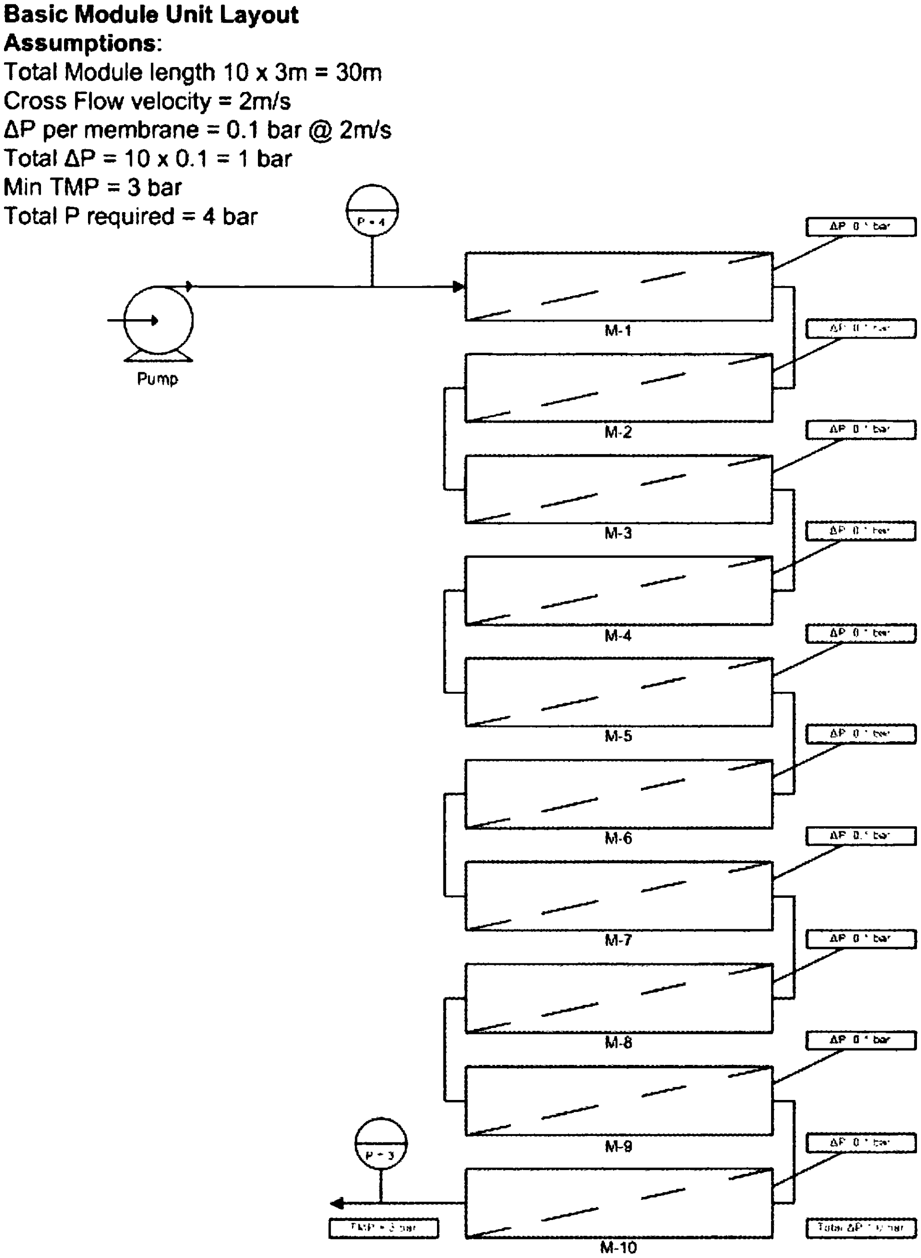
Over the range of suspended solids in the feed, 7 – 122 PPM, there was no effect of the feed flow rate on the filterability of the solution with consistently high particle rejection and similar flux values being measured. As is typical with high flow pressurised systems, the pressure drop along the membrane increased with increased flow. To ensure the optimum use of energy and membrane surface area, it is recommended that low flow rates, i.e. those approaching 2 m^3 h^{-1}, be used as a starting point in the initial optimisation of a full scale plant. By using lower flow rates, a positive effect has been seen on the amount of cleaning that is required to restore the membrane PWF after an experiment, such that at lower feed flow, less cleaning is required.

Work reported by *Chellam and Wiesner [110]* on polydisperse solutions suggests that cake morphology is a key variable that needs studying to gain a full understanding of the fouling layer build up on membrane surfaces. The effect of flow rate on cleaning can be explained by the sieving mechanisms experienced in polydisperse solutions and the increasing dependence of the fouling layer on the smaller particles within a solution. At the higher flow rates, the hydrodynamics of the feed being such that preferential migration of the smaller particles towards the membrane exacerbated by the high fluxes. Work done by [113] to determine the critical flux of a solution highlights the importance not just of transmembrane pressure but that flux rates can influence the particle deposition on the membrane and a balance exists that minimises fouling, supported by the findings here using a high flux membrane and a polydisperse solution over a feed transition between laminar and turbulent flow. At the higher flow rates, the increase in time to reach steady state and thus the slow build up of solute at the membrane needs further investigation to allow the optimal balance between all the controlling parameters in the filtration of a real polydisperse effluent.

8 Cost Benefit Analysis

8.1 Treatment of Waste Oil-in-Water Emulsion from a Cold Rolling Mill

A Cost Benefit Analysis (CBA) is prepared to calculate the cost per cubic meter of treated permeate. The following assumptions are used:



Basic Module Unit Layout
Assumptions:
Total Module length 10 x 3m = 30m
Cross Flow velocity = 2m/s
ΔP per membrane = 0.1 bar @ 2m/s
Total ΔP = 10 x 0.1 = 1 bar
Min TMP = 3 bar
Total P required = 4 bar

Figure 8-1 Basic Membrane Module layout using Tubular Membranes

Module Set-up:

- One module is equal to the maximum number of individual tubes allowed in series and has a length of 30 m.
- Length of each membrane = 3 m
- Maximum length of membranes in series = 30 m
- Number of membranes in series = 10
- Surface Area of each membrane = 0.2 m^2
- Total Module surface area = 2 m^2

Driving Force and Permeate:

- Average Specific Flux during operational run = 40 L m^{-2} h^{-1}
- Minimum Transmembrane pressure across any membrane tube = 3 bar
- Cross flow velocity across membrane surface = 2 m s^{-1} (3.65 m^3 h^{-1})
- Delta P across each membrane tube @ 2 m s^{-1} = 0.1 bar (see appendix A1)
- Total Pressure delivered per module = TMP_{min} + Delta P_{tot} = 3 + 1 = 4 bar
- Each module produces 80 L h^{-1} of permeate therefore 14 modules required to produce 1 m^3 of permeate for reuse and allow for one module to be going through a cleaning cycle whilst maintaining throughput.

Cleaning per module:

- Each membrane module will run for 24 hrs in between cleaning and each cleaning cycle will take 1 h to complete = 24 x 2 x 40 =1920 L of permeate
- A buffer tank can be used to store the effluent flow during the cleaning cycle.
- An initial flush of 50 L to remove initial waste build up.

- An alkaline rinse with a concentration of alkaline cleaner of 1 L m^{-3} into 100 L of distilled water
- Additional post alkaline flush of 50 L
- Acid rinse with ~ 0.5 wt% of Citric Acid into 100 L of distilled water
- Additional post acid flush of 50 L
- Total de-ionised water usage per cleaning cycle = 300 L
- Total Citric Acid (dry) usage per cleaning cycle = 0.5 Kg
- Total Alkaline Cleaner usage per cleaning cycle = 0.1 L
- Price of Citric acid = £0.60 / Kg (price via internet)
- Price of Alkaline cleaner = £1 / L
- Total chemical cost per m^3 = ((0.5 x £0.60) + (0.1 x £1)) / 1.92 = £0.21
- Total demin water cost @ £0.40 / m^3 = (0.35 x £0.40) / 1.92 = £0.08

Waste Flow rate to treatment plant:

- Average flow rate to plant of 2 m^3 h^{-1}
- Plant operates for 350 days to allow for down time (planned / unplanned)
- Approximately 330 cycles per year of treatment plant = ~ 8000 filtration hours
- Recovery rate = 90%
- Permeate produced = 14400 m^3 / annum

Power Requirements:

- Cost of 1 KW h = £0.08
- Pump efficiency = 75%
- Flow rate = 1.01 Kg s^{-1}
- Pressure required by pump = 4 bar

- Power required per m^3 = 7.5 KW

- Power required per m^3 per bar = 7.5 / 4 = 1.875 KW

- Electricity cost per m^3 = 7.5 x £0.08 = £0.60

Power Calculation Summary:

ΔP per module	0.1	bar
Number of membrane tubes	10	
Total ΔP across membranes	1	bar
Trans Membrane Pressure	3	bar
Pressure Drop Total	4	bar
Flow Rate / hr	3650	L / h
Mass Rate / sec	1.013889	Kg / s
Energy to pump per module	397.85	Watt
pump efficiency	75%	
Power / module	530.4667	Watt
Power / cub meter	7426.533	
	7.5	KW
Electricity cost	**£0.60**	m^3

Operator Man hours:

- Operator intervention in plant @ 1 h / day = 365 h / annum

- Hourly rate = £10 / h

- Total cost of operator = £3650 plus 10% = £4000 / annum

- Operator Cost per m^3 = 4000 / 14400 = £0.28

Summary of all individual costs per m^3:

Cleaning = £0.29

Power requirements = £0.60

Operator = £0.28

Total = £0.29 + £0.60 + £0.28 = £1.17 / m^3

Advantages:

- Reduction in the waste flow rate to flocculation and filter press by 90%.
- Increase in concentration of suspended oil should aid chemical treatment of the waste therefore leading to reduced chemical usage.
- Significant reduction in oily (treated) effluent being sent to discharge sumps.
- Production of a consistently low suspended solids and oil free permeate stream that would be ideal for feed into a low pressure reverse osmosis plant.

Disadvantages:

- Relative high cost of permeate stream when compared to the production of demineralised water from river water source.
- Due to the low annual permeate flow, labour costs are relatively high.
- Cleaning costs of the membranes are high.

Discussion

Costs could be lowered by reducing operator intervention and relying on more automated supervision of the plant, i.e. integrity tests after cleaning, and operators only becoming involved when issues are signalled. Annual savings in flocculation chemicals has not been factored in as this will be reduced significantly as well as the reduced cost of disposing of the oily filter cake from the filter press stage (the price for disposal of such waste at £21 / tonne was set by UK Government in 2006). The capital costs have not been considered in this study and would have an important influence on the overall economics of the process.

8.2 Treatment of Suspended Solids "Rich" effluent from Steel Making

A Cost Benefit Analysis (CBA) is prepared to calculate the cost per cubic meter of treated permeate of the filtration of a suspended solids rich effluent.

The following assumptions are used:

Membrane Set-up:

- Surface Area of each membrane = 6.1 m^2

Driving Force and Permeate:

- Average Specific Flux during operational run = 150 L m^{-2} h^{-1}
- Minimum Transmembrane pressure across any membrane tube = 2 bar
- Volumetric flow rate = 11.36 m^3 h^{-1}
- Total Pressure delivered per membrane = 2 bar
- Each membrane produces 915 L h^{-1} of permeate therefore 1.1 membranes required to produce 1 m^3 of permeate for reuse.

Cleaning per membrane:

- Each membrane module will run for 48 hrs in between cleaning and each cleaning cycle will take 1 h to complete (due to less percentage fouling seen during experiments) = 48 x 0.915 = 44 m^3 / cycle of permeate.
- An initial flush of 100 L to remove initial waste build up.
- An alkaline rinse with a concentration of alkaline cleaner of 1 L m^{-3} into 150 L of distilled water
- Additional post alkaline flush of 100 L
- Acid rinse with ~ 0.5 wt% of Citric Acid into 150 L of distilled water

- Additional post acid flush of 100 L
- Total de-ionised water usage per cleaning cycle = 600 L
- Total Citric Acid (dry) usage per cleaning cycle = 1.5 Kg
- Total Alkaline Cleaner usage per cleaning cycle = 0.3 L
- Price of Citric acid = £0.60 / Kg (price via internet)
- Price of Alkaline cleaner = £1 / L
- Total chemical cost per m^3 = ((1.5 x £0.60) + (0.3 x £1)) / 44 = £0.03
- Total demin water cost @ £0.40 / m^3 = (0.6 x £0.40) / 44 = £0.01

Waste Flow rate to treatment plant:

- Average flow rate to plant of 75 $m^3\ h^{-1}$
- Plant operates for 350 days to allow for down time (planned / unplanned)
- Approximately 330 cycles per year of treatment plant = ~ 8000 filtration hours
- Recovery rate = 95%
- Permeate produced = 570 000 m^3 / annum

Power Requirements:

- Cost of 1 KW h = £0.08
- Pump efficiency = 75%
- Flow rate = 3.16 Kg s^{-1}
- Pressure required by pump = 2 bar
- Power required per m^3 = 825 x 1.1 = 0.9 KW
- Power required per m^3 per bar = 0.9 / 2 = 0.45 KW
- Electricity cost per m^3 = 1 x £0.08 = £0.08

Power Calculation Summary:

Pressure Drop Total	2	bar
Flow Rate / hr	11360	L / h
Mass Rate / sec	3.16	Kg / s
Energy to pump per membrane	619.12	Watt
pump efficiency	75%	
power / cub meter	908	Watt
	1.0	KW
Electricity cost	**£0.08**	**m^3**

Operator Man hours:

- Operator intervention in plant @ 1 h / day = 365 h / annum
- Hourly rate = £10 / h
- Total cost of operator = £3650 plus 10% = £4000 / annum
- Operator Cost per m^3 = 4000 / 570 000 = £0.01

Summary of all individual costs per m^3:

Cleaning = £0.04

Power requirements = £0.08

Operator = £0.01

Total = £0.04 + £0.08 + £0.01 = £0.13 / m^3

Advantages:

- Low operating costs per m^3 of permeate
- Reduction in the waste flow rate to flocculation and effluent sump by 95%.

- Increase in concentration of solids should aid chemical treatment of the waste therefore leading to reduced chemical usage.
- Possible recovery of metals from the metal rich solids retentate.
- Production of a consistently low suspended solids and oil free permeate stream that would be ideal for feed into a low pressure reverse osmosis plant or for use where low solids content is required, e.g. run out table for hot slab surface spraying.

Disadvantages:

- Due to high flow rate of the effluent stream, a large surface area of membrane will be required.

Discussion

Due to the higher specific fluxes being obtained and the lower operating pressure of the membranes, the cost per cubic meter is significantly reduced when compared to the treatment of the oil-in-water emulsion. The capital costs have not been considered in this study and would have an important influence on the overall economics of the process due to the large membrane surface area required to treat the estimated flow rates.

9 Conclusions and General Discussion

9.1 Conclusions

- Ultrafiltration of a waste oil-in-water emulsion from a cold rolling mill using both tubular PVDF and hollow fibre PAN membranes, produced a quality of permeate that was suitable for a variety of different reuses within a steel works and is independent of the feed water oil concentration. The quality of permeate is very similar to Afan river water during summer months.

- Cleaning is key to the longevity of the membrane processes and will affect the operating costs of a full scale plant. Repeated cleaning can lead to shorter life expectancy of the membranes. This balance between cleaning and its intensity is a major component of the economic feasibility of a membrane water treatment process.

- Tubular PVDF membranes proved more robust to both the operating and cleaning conditions exerted upon them when compared to the PAN hollow fibre module during the filtration of waste emulsion.

- Significantly higher fluxes obtained during the filtration of the prepared emulsion suggests that segregation of the effluent produced from cold rolling should be investigated to prevent any pick of contaminants from nearby sources that may have a negative effect on filtration.

- The operating cost per cubic meter of permeate from a tubular ultrafiltration plant treating a waste oil-in-water emulsion from a cold rolling mill using Koch membranes is £1.17. Over 50% of the operating cost is due to the electricity consumption, plans within Port Talbot Works to consider the greater use of indigenous fuels could, in the future, reduce electricity costs.

- The operating cost per cubic meter of permeate from a hollow fibre ultrafiltration plant treating a suspended solid rich effluent from a steel making process using Koch membranes is £0.13.

This work has investigated the application of membrane water treatment processes to treat two real effluent streams within an integrated steel works and a predefined oil-in-water emulsion. Time spent with the Energy Department allowed the identification of the two effluent streams based on their impact on water usage or difficulty of treatment. The waste emulsion is from a cold rolling mill and is a source of oil contamination in the resulting final effluent that is discharged to sea. The particulate stream, steel plant off gas scrubber water, has a large flow and variable contamination loading.

To be able to assess independently the use of membrane processes, an experimental rig was designed, constructed and commissioned to carry out the experimental section of the study. By designing a flexible pilot plant, this allowed investigation into the major operating parameters that effect the separation, as well as different membrane module formats and materials. This was achieved by conducting experiments on sampled wastes using commercially available full size membrane modules.

Time with the Energy department highlighted the huge range of qualities and quantities of water used within steel making whilst giving me first hand exposure to water treatment technologies. Due to the relative high costs of designing and building a pilot scale rig to investigate NF or RO processes, it was decided that the area of membrane separations that would investigated was to be micro / ultra filtration.

9.2 Selection of Waste waters

During the initial time spent within the Energy department, it was apparent that the cost of water treatment and abstraction for the majority of water qualities was minimal. This pushed the focus to effluents that have large costs associated with their treatment and disposal, or an effluent with a large flow rate that is not reused. Current treatment of the waste emulsion is both expensive and unreliable; it is a manned plant and has very little automation. Due to the ease of membrane process plant automation and their ability to produce a consistent permeate quality; this seemed an ideal stream to select.

The gas scrubber effluent was selected due to its variability in concentration of particulates of small diameter consisting largely of metal oxides. This deemed them difficult to treat using coagulation and flocculation techniques and online continuous monitoring would be needed to optimise the use of polymer flocculants. The membrane process is able to treat variable feeds without the addition of chemicals and that sufficient monitoring technology used in conjunction with a modern control system allows a fully automated self-optimising plant to be constructed and operated. The issue of manning levels is one that is always in the forefront of large modern manufacturing.

9.3 Significance of the work

This work has shown that membrane processes are able to treat real waste streams from a large steel works reliably and produce a quality of permeate that is suitable for many further uses. It has produced flux and operational data using commercially available membranes in available size formats, on streams that have otherwise not been investigated. Although due to the uniqueness of every effluent, this data can only be used as a guideline for possible attainable flux rates using commercially available membranes.

Of the two different wastes treated in this research project, the application of membranes to the treatment of oil-in-water emulsions has shown the most promise. The scrubber effluent would require large capital outlay just for the membranes. Due to the high cost per square meter of PVDF and its large footprint, the hollow fibre PAN module needs further investigation; to expand the limited amount of data available in relation to cleaning regimes and long term membrane performance. The fact that the membrane experienced significant fouling due to a routine citric acid rinse, raises doubts about its resilience and robustness in the process within the challenging environment of a steel works.

Differences between the prepared emulsion and the actual waste have highlighted the importance of being able to treat the waste at source to minimise the pick up of variable contaminants. It has been demonstrated that the membranes are able to treat wastes with variable composition, but optimisation is consequently rendered difficult.

9.4 Future Work

- Development of process models for both water system and membrane processes.

This would allow simulations to be undertaken that could identify effluent streams that have the largest potential impact on the water / energy system. Incorporating membrane models into the simulations, allows initial work to be done that can estimate the effectiveness of the process, operating costs and in some cases, eliminate streams from consideration before more expensive pilot plant work is undertaken. Work is being undertaken by corus to install more flow metering that would facilitate this in the future.

- Use of membranes to significantly concentrate the waste cold mill oil/water emulsion and therefore enhance the existing emulsion breaking techniques.

Membrane treatment does not obviate the need for further emulsion processing. The combination of a membrane stage to concentrate emulsions to feed traditional chemical emulsion breaking processes may provide an aqueous permeate stream for reuse. A large proportion of the waste (emulsion) produced by the current treatment process consists of water. By reducing this volume in the emulsion, the amount of oily sludge that needs disposal would be reduced.

- Previous work has shown the viability of a combined UF / RO plant.

Due to the consistently high quality of permeate produced by UF on what is essentially a low conductivity stream, ~ 200 micro siemens, a combination of UF and RO would show synergies between the high levels of oil and particulate removal from UF and the operation of the RO membrane. The works demand for up to 200 $m^3 h^{-1}$ of demineralised water is far greater than could be recovered from effluent. However, a local requirement for demineralised water, could be partially recovered by emulsion concentration.

Membranes have shown that they can offer reliable treatment of effluents produced by a steel works. At current costs of water to Port Talbot, the feasibility of membranes to offer a competitive alternative to traditional treatment processes is, at present, questionable. The integration of membranes into a steel works will be of use if future water costs or government legislation force adoption of cleaner processes and recycle / reuse technologies so that abstraction from raw water supplies can be significantly reduced.

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Appendix – Hydrodynamics of Koch Tubular Membrane

KOCH
MEMBRANE SYSTEMS™

ABCOR® - FEG™ PLUS MODULE: 5-HFP-276-PVI

Industrial Tubular Ultrafiltration One-Inch Modules

PRODUCT DESCRIPTION

KMS Part Number (KPN):	0711660
Membrane Chemistry:	PVDF
Membrane Type:	HFP (negatively charged)
Membrane Area:	1.1 ft^2 (0.10 m^2)
Molecular Weight Cut-off:	120,000 Dalton (nominal)
Housing Construction:	CPVC
Seal:	CPVC Insert (Epoxied in Place)
Gasket:	Viton®
Interconnecting Components:	See Reverse

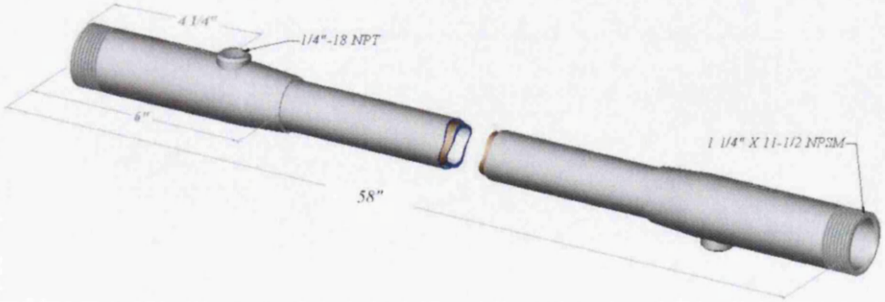
RECOMMENDED OPERATING LIMITS[1]

Maximum Inlet Pressure:	90 psi @ 140°F (6.2 bar @ 60°C)
Minimum Outlet Pressure:	5 psi (0.3 bar)
Maximum Operating Temperature (at pH 8.0):	140°F (60°C)
Maximum Permeate Side Back Pressure:	5 psi (0.6 bar)
Maximum Feed Side Pressure Drop:	5 psi @ 140°F (0.7 bar @ 60°C)
Allowable pH - Continuous Exposure:	2.0 - 10.0 @ 140°F (60°C)
Allowable pH - Short Term Exposure:	1.5 - 10.5 @ 140°F (60°C)

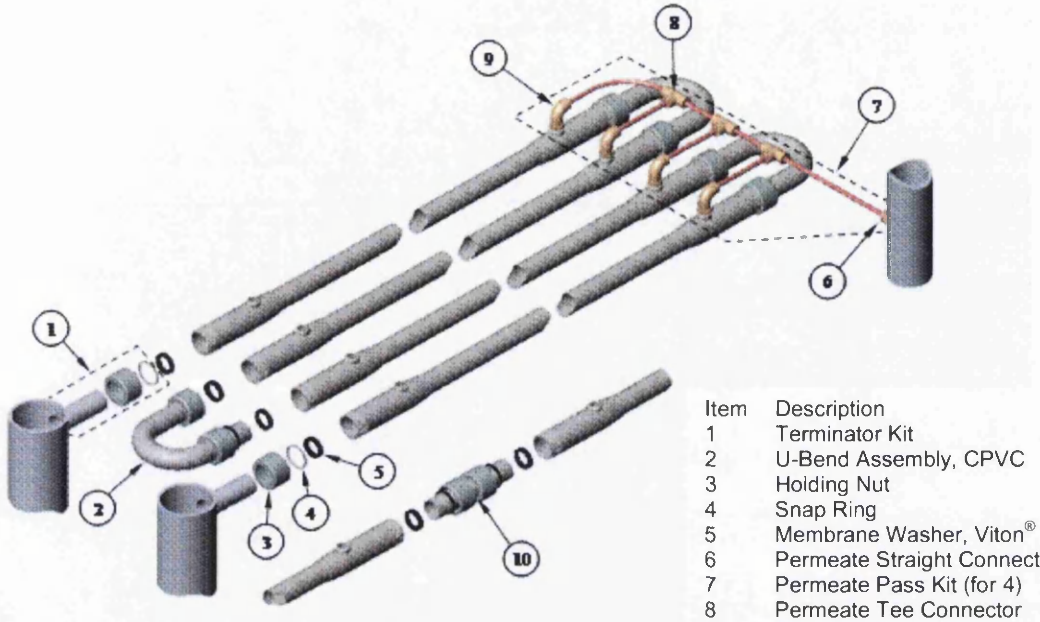
FEED FLOW VS. PRESSURE DROP

Circulation Flow		Crossflow Velocity		Pressure Drop	
gpm	m^3/hr	fps	m/s	psi	bar
19	4.3	7.8	2.4	1.0	0.07
30	6.8	12.3	3.7	2.2	0.15
38	8.6	15.5	4.7	3.0	0.21

PRODUCT DIMENSIONS



ANCILLARY PARTS[2]



Item	Description	KPN
1	Terminator Kit	0230020
2	U-Bend Assembly, CPVC	0020392
3	Holding Nut	0020281
4	Snap Ring	0020310
5	Membrane Washer, Viton®	0020375
6	Permeate Straight Connector	0211860
7	Permeate Pass Kit (for 4)	0211786
8	Permeate Tee Connector	0211803
9	Permeate Elbow Connector	0211804
10	Interconnector Kit, CPVC	0020456

MEMBRANE INCOMPATIBILITY[3]

Aprotic Solvents (Dimethyl Formamide, Dimethyl Acetamide, N-Methyl Pyrolidine, etc.)
Chlorinated Solvents (Methylene Chloride, chloroform, Carbon Tetrachloride, etc.)
Ketones (Acetone, Diacetone Alcohol, etc.)
Silicones or Silicone based Defoamers (Siloxane)

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[1] Koch Membrane Systems, Inc. must review operating and cleaning conditions for all new plants as well as changes to any existing plants. Data based on Water at 77° F and a specific gravity of 1.0. Circulation rates exhibit variances of 15%.

[2] KMS recommends that these membranes be used with KMS supplied ancillary parts. Sealing is provided by o-rings and gaskets. No additional sealing compound or tape is recommended for use on threaded connections.

[3] Prior to exposing the membranes to any chemical, the chemical should be reviewed by Koch Membrane Systems, Inc. Aside from the listed chemicals, synthetic coolants, semi-synthetic coolants, kerosenes, naphtha, gasoline, floc polymers, etc., may affect membrane performance.

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