APPLICATION OF MEMBRANES TO TREATMENT OF WATER BASED EXPLORATION AND PRODUCTION WASTES

A Dissertation

by

OLUWASEUN ALFRED OLATUBI

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

August 2009

Major Subject: Civil Engineering

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ABSTRACT

Application of Membranes to Treatment of Water Based Exploration
and Production Wastes. (August 2009)

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Produced water and spent drilling fluids from petroleum operations represent a significant expense to companies developing new energy reserves. These spent fluids, seldom recycled, offer a viable source of water resources for oil-field reuse. A major obstacle to reuse is the presence of suspended solid material in the fluids. Such contaminants, if not removed, will not only prevent any reuse but will also impede disposal. The objective of this project was to evaluate membrane filtration as a way to remove suspended and entrained particles to produce re-useable effluents using membranes. Ceramic and Polyvinylidene Flouride (PVDF) hollow fibre membranes were used in laboratory scale experiments in the investigation of the colloidal filtration of field produced spent drilling fluids and produced water.

Feed parameter and operational parameter evaluation of ceramic and PVDF hollow fibre membrane filtration of spent drilling fluids and produced water showed that feed concentration, solids in the spent drilling fluid and oil in the produced water, is the most important parameter during membrane filtration. Operational parameter variation showed that high cross flow velocity was beneficial in flux maintenance during spent drilling fluid filtration due to its high solids concentration because of the scouring effect on the cake layer on the membrane surface. Pressure regimens were important in flux decline as relatively high pressures accelerate the consolidation of the concentration polarization layer causing flux decline. High temperatures were generally beneficial for increased flux in the filtration of produced water and spent drilling fluids.

Resistance calculations were used to deduce the contribution of individual resistances during the ceramic filtration of produced water and spent drilling fluids and were identified as a real-time tool for monitoring membrane integrity and fouling. Backwashing as a fouling mitigation technique was effective in flux maintenance in ceramic membranes especially in the filtration of produced water; cleaning solutions were effective in flux recovery in ceramic membrane filtration and to a slightly lesser degree in hollow fibre membrane filtration. A methodology in determining the suitability of water based oil field wastes using membranes was developed to help future investigations of this type.

DEDICATION

To my God and my god. God the Almighty, the Father of the fatherless. My god, my mother Agnes Omodunke Olatubi

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I am grateful to a host of people certainly too many to mention unless I choose to write a whole dissertation thanking them, but to all friends and family through these years and journeys I am eternally grateful. For special mention, I am very grateful to my committee chairs and members; Hann Roy Jr., David Burnett, Jean Louis-Briaud, Jerome Schubert and Ron Kaiser for all their guidance through this journey. I am grateful to GPRI staff especially Connie Connaway and to Carl Varvra and the Separation sciences team that showed me the ropes these years.

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CHAPTER I

INTRODUCTION

1.1 Introduction

Exploration and production (E&P) operations in the oil industry are usually large scale operations that produce large footprints ecologically. Over the years the challenge to the oil and gas industry has been to minimize the foot print of its operations to fit the growing public and regulatory environmental consciousness as well as provide good stewardship to the environment. To this end the Department of Energy (DOE), academia, oil producing companies, oil servicing companies, regulatory agencies, environmental groups and other stakeholders formed the Environmentally Friendly Exploration and Production program. This initiative is designed at integrating advanced technologies into systems that significantly reduce the impact of petroleum drilling and production in environmentally sensitive areas.

The objective of this program is to identify, develop and demonstrate cost effective technologies that reduce environmental tradeoffs that may allow operations in environmentally sensitive areas that are currently off limits. The Environmental Friendly Exploration and Production group decided in its first phase to focus on making drilling more environmentally friendly. To this respect the Environmentally Friendly Drilling (EFD) initiative arose as a subset of the Environmentally Friendly Exploration and Production program. The EFD is focused on developing and demonstrating cost effective technologies that reduce the footprint of drilling operations and in doing this defined some broad criteria about the environment and technology. It ruled that every environment is to be viewed as sensitive, that technologies that reduce footprint of drilling operations sustainably shall be investigated and developed.

This dissertation follows the style of the Journal of Membrane Science.

The issue of water based wastes particularly produced water and water based drilling fluids is an area of interest to the EFD. The management and disposal of these wastes (produced water and water based drilling fluid) creates large footprints in E&P operations and is of environmental concern due to low amount of recycle and re-use apart from the burgeoning issue of freshwater scarcity. The EFD in tackling these wastes set out to first reduce the footprint of these wastes and also increase the amount of re-use in either oil and gas operations or for non oil field or related non-consumption uses. To this effect this thesis is an investigation into one of the technologies aimed at reducing the footprint of water based wastes and increasing their re-use for oil-field applications.

The objective of this thesis is the investigation of membrane technology in the treatment of produced water and spent water based drilling fluids in order to achieve colloidal and suspended particle filtration. This thesis also aims to achieve volume reduction of the wastes and at the same time produce effluents that could be re-used in oil-field applications. This thesis puts forward the hypothesis that solids (colloids and suspended particles) removal from water based wastes in the colloidal and particle range made possible by using membranes is a key step to re-use and waste volume concentration. It investigates using membrane technology to provide empirical evidence of filtration of water based exploration and production (E&P) wastes in producing effluents that can be re-used.

1.2 Introduction to Drilling

In the exploration and production of oil and gas, the act of drilling commences after various pre-drilling activities such as seismic evaluation, reservoir evaluation, drilling program design, and other well development and production activities needed to ensure successful exploration and production. Drilling primarily entails the use of a drilling bit to make a hole. In drilling for oil and gas the hole could be drilled for various reasons, it could be to discover new petroleum reserves (wildcat) or to exploit known petroleum reserves (development well). Development wells are the types of wells referred to throughout this thesis [1].

Drilling can occur offshore and on-shore. Offshore being in territorial waters notable, worldwide offshore drilling locations include the gulf coast in America and the North Sea in Europe. Onshore drilling on the other hand involves drilling on land, there are more onshore drilling operations worldwide than offshore drilling operations for various reasons chief amongst which is cost as considerable resources are mobilized and expended in offshore drilling operations. Offshore exploration and production is primarily executed by multinational corporations and national governments while onshore drilling though capital intensive is relatively inexpensive and is carried out by various interests from independent producers to corporations.

Various equipment are used in drilling operations and could be generally classified based on their function, they include drilling rigs, rig power equipment, hoisting equipment , circulating system equipment and rotary system equipment. A drilling rig is a machine used to drill the wellbore [2], it usually entails every equipment in the drilling process apart from the living quarters. Onshore drilling rig types includes the conventional rig or the mobile rig such as the Jackknife or Cantilever rig while offshore rig types are either the bottom support type rigs such as the Jackup rig or the floating type rig such as the semisubmersible rigs or the drill ships. Rig power equipment consists mainly of the internal-combustion diesel engines which could either be the diesel-electric type or the direct-drive type [2], their basic function is to generate power for drilling operations. Most rig power is consumed by hoisting and fluid circulation system, and total power requirements for most rigs is between 1,000 to 3,000 hp [2].

Rig hoisting equipment include the derrick and the block and tackle which consists of the draw works, the crown block, the travelling line, the anchor, storage reel and the drilling lines. Hoisting equipment function in raising and lowering of drill strings, casing strings and other associated drilling equipment inside and outside the hole. The rig circulating system equipment includes the mud pumps, mud mixing equipment, solids control equipment such as centrifuges, hydrocyclones and other contaminant removal equipment. The circulation system functions primarily to pump drilling mud and for the removal of solids. The rotation of the bit could be achieved using a conventional rotary table and Kelly system which includes equipment such as the Kelly, Kelly bushing, rotary drive, rotary table and swivel or a topdrive system could be used in which hydraulic or electric motors are used for achieving bit rotation. The Kelly systems are more common in most onshore drilling rigs in America. Figure 1.1 shows the schematic of a rotary drilling rig.

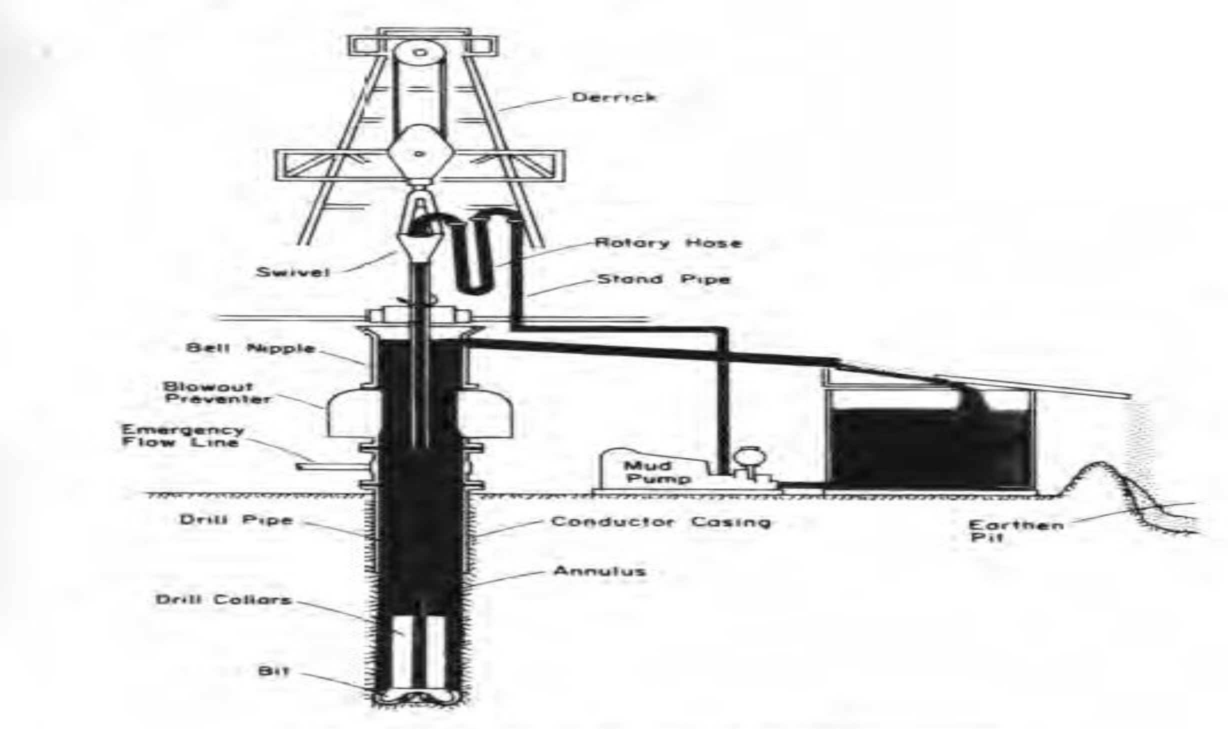


Fig. 1. 1 Schematic of a rotary drilling rig [2].

In the last thirty (30) years drilling technology has gone through significant technological changes resulting in smaller rigs but wider subsurface reach. Innovations such as horizontal drilling i.e. drilling where the well bore is more than eighty degrees (80^0) from the vertical has helped reduced significantly surface disturbance of drilling activities while still enabling the optimization of oil and gas exploitation. Figure 1.2 show us the progress made in rig sizes in the last thirty years, it shows a seventy percent (70%) reduction in rig size and a six thousand four hundred percent (6400%) increase in the subsurface drillable area for wells with about 10,000 ft depth.

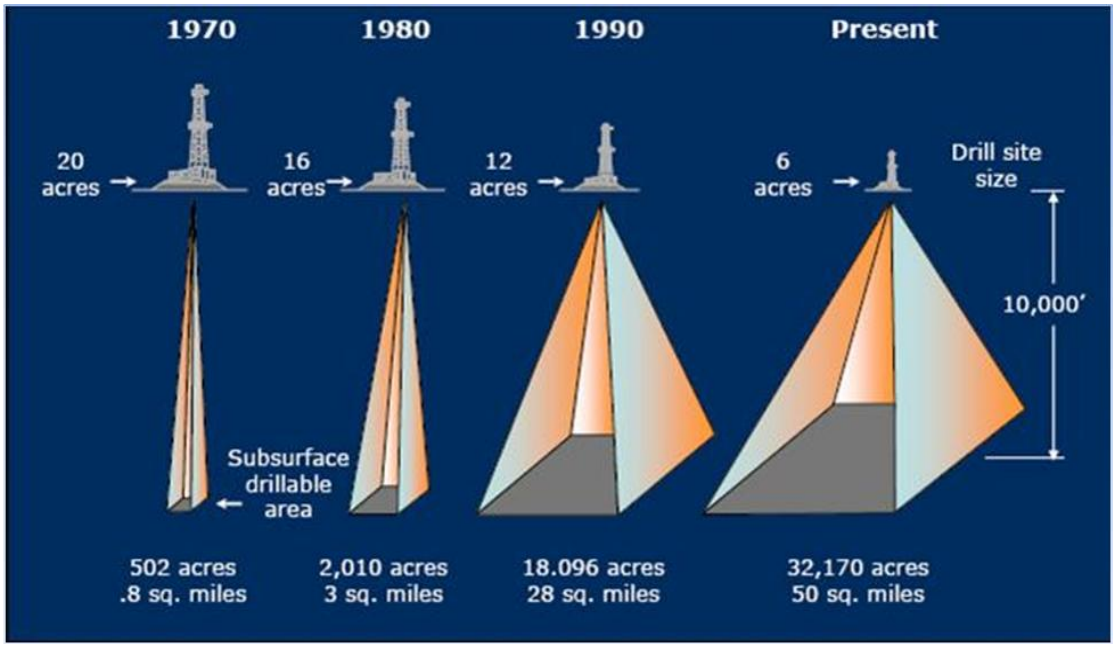


Fig. 1. 2 Subsurface reach and rig sizes in the last thirty years [13].

Though this surface reduction translates to less surface area or ecosystem disturbance in drilling operations, the wider subsurface reach means that there would be an increase in the amount of drilling wastes generated due to increased subsurface reach. In handling wastes generated from this wider subsurface reach the gains made in surface reduction are offset as waste holding, hauling and treatment facilities such as reserve pits increase the total surface area associated with drilling operations significantly impacting the environment in this present age than thirty (30) years ago.

To achieve reduced impact of drilling operations, technological innovations or practices that make rigs smaller would not reduce the impact or footprint of drilling operations alone if there are no corresponding technologies to deal with compacting the waste volume generated by wider subsurface reach. To optimize smart rig technology and drilling practices, there is a need to investigate and develop technologies that promote waste volume reduction, recycling and re-use of water based wastes rather than improving disposal technologies such as slurry or produced water injection.

1.3 Energy and Future Demand

The energy question is increasingly becoming the most important question of this present age, with growing populations especially those of South East Asia and their attendant energy demand the issue of energy has been thrust as a front burner issue globally. The search for energy to meet present demands and future forecasts is becoming more intense and more diversified than ever as alternative energy sources are vigorously investigated. Sources such as renewable fuels, solar energy, wind energy, geothermal energy and hydrogen are being developed to meet the growing energy needs worldwide.

Despite this diversification of sources to meet the global energy demand, wholesale adoption of alternate energy sources have limitations either due to cost, scale, newness of technology, reliability and or efficiency. These challenges faced by alternate energy sources still makes crude oil and coal the prime energy sources today. The relative low cost of coal and crude oil, widespread use and technological advancements in their exploitation makes them very competitive. Despite the huge drive towards alternative sources of energy, exploration and production activities regarding oil has increased dramatically in the past five years with crude oil barrel prices hovering near $100 dollars per barrel in the summer of 2008 compared to about $12-$13 per barrel a decade ago [3].

The Exploration and Production (E&P) industry is expected to witness significant growth through the year 2020. Conservative projections estimate the expected growth not to be less that 1.5 % per year with the most probable projections bordering on 2% per year [4]. Average prices are expected to rise at a higher rate over the next 10-15 years than over the past 10-15 years signifying increased opportunities and capabilities in the oil industry as the opportunity for substantially more revenues per barrel of oil equivalent is produced [5]. Projections for demand for petroleum products is upward, gas consumption in the US will increase by 41% from 2000 to 2025 while oil consumption would increase by a smaller margin, 27%, during that same period [4]. Rig count is currently on the rise [6].

Conservative projections show that globally oil demand would continue to rise particularly in South East Asia and developing economies. Social and economic changes would drive demand for more modern conveniences such as automobiles, electrical appliances and travel all fueled by the vast global communication expansion which would result in greater energy usage. It is expected that by the end of the decade the demand for oil will be nearly 100 million barrels per day [7]. For the US, currently the largest energy consumer in the world, these consumption trends translates to increased competition for global energy markets as studies show that oil rich nations are using more energy and cutting exports [4] due to increasing needs in their nations shrinking available exports to traditional customers such as the US.

This increased global energy demand is leading to increased exploration and production activities (E&P) worldwide. Statistics from the American Petroleum Institute (API) show that there are about 1,801 active rotary rigs in the US as of November 2007 compared to a 2006 average of 1,649 [6]. Due to increasing natural gas demand, the Energy Information Administration (EIA) projects that 22,000 gas wells will have to be drilled by 2020 up substantially from the 15,200 wells successfully drilled and completed in 2000 [8]. This increased drilling activity is not confined to the US but is global, as increased drilling activities are evident in all producing regions worldwide. There is also a recognizable growth in increased stimulation techniques for existing oil wells to maximize yield as there continues to be further development and research into stimulation techniques for greater oil and gas recovery.

Increased demand for energy and rising energy prices have renewed interest in unconventional oil resources. Unconventional oil resources is an encompassing term for oil resources that are generally more challenging to extract than conventional oil, examples are tar-sands, heavy-oil, bitumen and oil-shale. Unconventional hydrocarbons are usually situated in tight, low permeability, low porosity, low recovery, difficult to produce rock formations such as shales, chalks, tight sands and coal seams[9]. These rocks require special stimulation, completion and or production technologies to extract their hydrocarbons. Significant improvements have been made in extraction technologies of unconventional reserves. Notable examples of significant unconventional oil extraction are the Orinoco extra-heavy oil belt where Venezuelan extra heavy oil production grew from about 80 million barrels in 2000 to about 240 million barrels in 2005 and Western Canada where Canada has boosted its bitumen production from 210 million barrels in 2000 to a little more than 400 million barrels in 2006 [9].

Unconventional oil is projected to play a significant impact in meeting the rising global energy demand. As demand grows in the US and globally it is predicted that unconventional oil resources shall increasingly become important in meeting future energy needs. Current estimates of some 7.5 trillion barrels of in-place bitumen, extra-heavy oil and shale oil are over three times greater than the 2.25 trillion barrels of recoverable conventional oil estimated to have been discovered to date. Estimated in-place resource of these unconventional oil is about seven times greater than the estimated recoverable conventional liquids from field growth and yet to find sources. Also with the exception of gas hydrates, estimated in-place volumes of unconventional gas are estimated to be an average of four to five times greater than the estimated recoverable gas from field growth and yet to find sources [9].

These reserves represent significant resources and they also represent a technology dividend. As more interest is generated in these reserves vast technological improvements are needed to expedite exploitation beyond their current state. Though these reserves are estimated to be able to add about 400,000 barrels of annual new production they are still a far cry from the required five to six million barrels a year needed to meet expected rising global demands in the face of depleting existing reservoirs. It is expected that technology would have an increasing role in exploiting newer deposits and also allow the efficient use of resources in the exploitation of new and existing reservoirs.

From figure 1.2 it is clear that though rig sizes have reduced over years, to offset the effect of the impact beneath the surface caused by extended subsurface reach commensurate technological development is needed to handle the wastes generated. In the exploitation of unconventional resources the dynamics are markedly different as copious amounts of resources such as freshwater is needed for their successful exploitation. Also copious amounts of wastes are generated in their exploitation, wastes such as fracture fluid backflow and produced water. In the exploitation of unconventional resources optimal use and recycle of resources and waste is paramount not only to reducing environmental impact but also for financial exploration viability.

For example, hydraulic fracturing, a stimulation technique routinely used on oil and gas wells in low-permeability reservoirs is a widespread stimulation technique used in exploiting some unconventional reservoirs. Hydraulic fracturing involves pumping water and some suitable proppant at high pressure to create and propagate a fracture in the surrounding rock formation downhole. These fracturing operations are known to consume large volumes of freshwater to induce the fracture and they also generate large volumes of fracturing (frac) waste in their flow back after fracturing these formations. Fracturing operations consume millions of gallons of fresh water and generate millions of gallons of fracture fluid backflow in wastes [8,9].

As some unconventional sources require large freshwater resources in their exploitation in some cases such as coal bed methane reservoirs, produced water is generated before they can be exploited. Coal Bed Methane (CBM) is an unconventional oil source where beneath the earth methane is adsorbed to crystalline surfaces of coal due to hydrostatic pressure of overlying water in the coal beds [10]. To strip the methane off the crystalline surfaces the water needs to be pumped out, thus unlike conventional oil fields where produced water is generated as the field matures the reverse is the case with CBM produced waters. Without a doubt unconventional resources are central to meeting the global energy demand, the environmental implication of freshwater use and produced water generation remains the abiding question technology must address to allow for sustainable exploitation of natural resources to meet the global energy demand.

1.4 Waste Description

There are three main categories of wastes associated with exploration and production activities, they are produced water, spent drilling fluid and associated wastes [11]. Produced water is defined by the Environmental Protection Agency (EPA) as “Water brought up from hydrocarbon-bearing strata during the extraction of oil and gas, and can include formation water, injection water and chemicals added downhole or during oil-water separation process” [12]. Produced water includes components such as organic chemicals, salts, hydrogen sulfide, heavy metals, hydrocarbons and other various components primarily dictated by the geologic features of the reservoir where they are produced. In discussing produced water an associated term used frequently is “water cut”, water cut is defined as the ratio of produced water to the volume of reservoir fluid produced. This ratio could range from less than 1 to about 40 depending on the maturity of the field [13]. Average US cut-out ratio is estimated between 7–10 barrels of produced water for 1 barrel of oil produced [10,13].

Spent drilling fluid is made up of the drilling fluid and rock cuttings. Drilling fluid could either be water based, oil based or synthetic based depending on the continuous phase which could either be freshwater, diesel or synthetic oil respectively. The drill solids are crushed rock formation generated by the drilling bit when drilling the hole. Spent drilling fluids could have solids concentration of upwards of 20,000 mg/L. The nature of the solids is completely dictated by the formation while the sizes of the cuttings are determined by the bit characteristics and rate of penetration of the bit [2]. For a water based mud, the continuous phase is either fresh water or brine, but to facilitate the primary function of the drilling fluids which is primarily to suspend the cuttings and pressure maintenance chemicals are added to the continuous phase to perform specialized functions.

To make the drilling fluid heavy, weighting materials that do not react with the water are added, examples of such materials are barite and galena. To increase viscosity reactive solids predominantly clays are added, common examples are bentonite, attapulgite and various synthetic polymers [1]. To avoid loss of the fluid to the sub-surface filter cake forming additives and fluid loss prevention additives are added to the water such as starches, lignosulfonate and carboxymethyl cellulose. Thus, the formulation of a drilling fluid is complex and dependent on the formation being drilled and functions required of the drilling fluid. Significant progress has been made towards environmentally friendly drilling fluids incorporating benign and easily biodegradable fluid constituents.

The final waste category, associated wastes includes various small waste streams that are connected to specialized E&P operations, examples of associated wastes include completion fluids, work over or stimulations fluids, tank bottoms, dehydration or sweetening unit wastes, used solvents or degassers, cooling water, used oils, untreatable emulsions and a host of wastes streams [11]. They are generally not produced as much as other E&P wastes and usually need some form of specialized handling or treatment for their disposal. This research does not focus on associated wastes as they are quite varied and not significant in proportion to the total volume of wastes generated in E&P operations.

1.5 Water Based Wastes Management

Produced water comprises approximately 98% of the total volume of E&P wastes generated [14]. Approximately 18 billion barrels of produced water was produced onshore in the US in 1995, compared to 148.7 million and 20.6 million barrels of drilling wastes and associated wastes respectively produced onshore in the US in the same year [11]. These figures exclude the additionally large volumes of produced water generated in US offshore operations. From disposal statistics available 71% of produced water is used injected for Enhanced Oil Recovery (EOR) and pressure maintenance in the reservoir, 21% is injected into disposal wells while 3% is discharged and 2% re-used. For drilling wastes 47% is evaporated on site, 21% buried on site, 13% is injected into disposal wells, 7% is re-used for drilling, 2% is hauled off-site, 1 % is landspread. For the associated waste streams 52% is sent to treatment facilities, 14% is incinerated, 12% is evaporated from pits and landspread, 7% is disposed by injection and 7% is recycled or reused [11,14]. See figure 1.3.

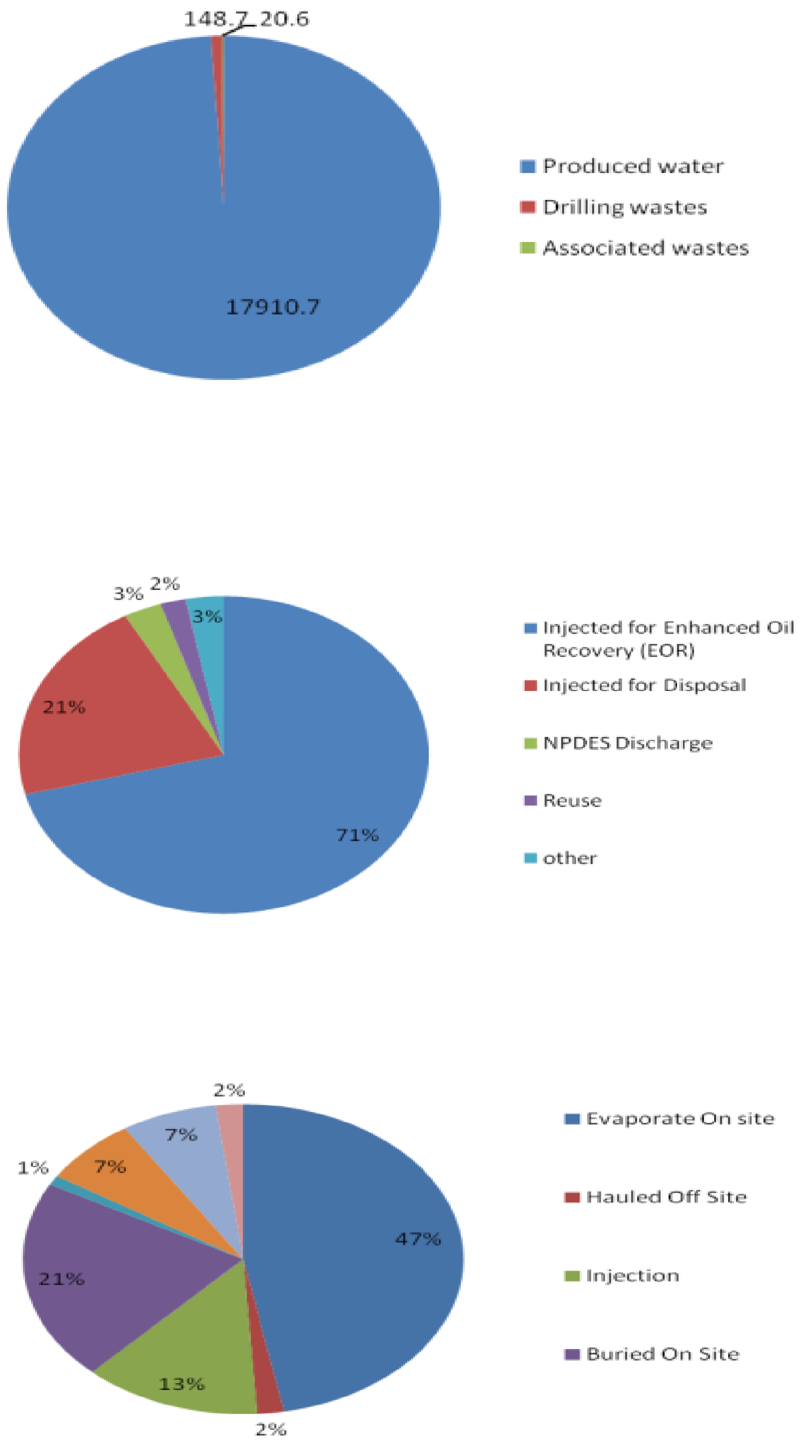


Fig. 1. 3 Waste disposal statistics.

Management of wastes generated from E&P operations represents a significant cost to those in the industry. Cost of treatment and disposal of produced waters could range from about \$0.15 - \$15 per barrel of produced water amounting to a global industry cost of \$50 billion per year [13]. Commercial disposal of oil based mud cuttings and cuttings disposal range from \$2-\$40 per barrel and \$0.50-\$40 per barrel for water based fluids and cuttings disposal. For associated waste such as tank bottom disposal costs range from about \$0.85-\$40 per barrel [15]. All these costs do not include transportation or trucking costs which could increase the costs of disposal and treatment significantly.

Most of the disposal and treatment costs have to do with disposal methods such as injection (for produced water and drilling waste) and do not in any way recover the produced water and spent drilling fluid for re-use or recycle. Apart from the disposal costs, costs associated with acquiring fresh water resources are increasing as operations such as hydraulic fracturing are straining municipal water supplies [16]. Using the Permian basin as an example, about 390 million gallons (9.3 million barrels) of water per day go into re-injection disposal and less than 1% of this is recycled, such prodigious use of scarce freshwater sources is bound to have socio-political implications evident in “water wars” in places like Colorado and Texas [17].

1.6 Freshwater Sources

Freshwater sourcing is becoming rather difficult especially for the exploration and production of oil and gas. There is increased awareness about water use in areas where unconventional resources are located as these areas are already challenged for freshwater. Operators in areas exploiting unconventional reserves such as the Barnett Shale in Texas and the Rocky mountains in Colorado are increasingly facing stiff competition from municipal communities and ranchers over freshwater use. Although agriculture (irrigation) still consumes the largest portion of freshwater in most communities [18], there is an increasing concern over the non-sustainability of fresh water use in E&P operations due to the low-levels of recycle and re-use especially in the light of agricultural practices streamlined to effectively conserve freshwater. For example in Alberta, Canada with approximately 9.7 billion m^3 of freshwater, 4.5 billion was allocated to irrigation and approximately 0.5 billion m^3 was allocated to the petroleum industry, there was about 0.6 billion m^3 produced water after operations and approximately half was injected for reservoir maintenance and waterflood while almost 0.3 billion m^3 was injected into disposal wells [18].

Freshwater sourcing is increasingly becoming a challenge for E&P operations as freshwater costs are becoming a significant part of operating costs. It is not uncommon for operators in the Barnett Shale to truck freshwater from over one hundred and one hundred and fifty miles to their drilling locations as fresh water prices have increased steadily over the last five years [personal communication]. These challenges are also becoming evident as regulations being promulgated by local communities and regulatory bodies reflect the need to protect freshwater sources not from contamination as it was traditionally framed but also from “excessive use”. Regulatory bodies are exploring ways to force behavioral shifts in water use not only by the industry but from all stakeholders [17].

Social issues indirectly related to freshwater sourcing and produced water and water based drilling fluid disposal are also gaining traction amongst stakeholders. Hauling in of freshwater and hauling off of the drilling wastes and produced water for disposal from drilling sites expose communities in areas where drilling operations occur to high levels of noise due to the constant vehicular traffic. For a fracture operation more than three hundred trucks (300) could be used to haul the wastes. Recent social studies by Gene Theodore [19] in the oil producing areas of the Barnett shale show that communities are increasingly becoming exasperated at these “inconveniences” even though royalties from the industry represents a large portion of the tax-base of these communities.

1.7 Conventional Management Options

In the previous sections the classification of water based E&P wastes, volume of the wastes generated, disposal and treatment percentages and freshwater sourcing was highlighted. In this section some general conventional technologies used in the disposal and treatment of this E&P wastes shall be discussed. The discussion shall start with a brief description of each technology, its advantages, limitations, cost implications and an evaluation based on the most important objective of the EFD aside from efficiency i.e. low footprint and increased re-use and recycle. Technologies aimed at spent drilling fluid disposal or treatment shall be discussed first and technologies aimed at produced water disposal or management shall be discussed after.

1.7.1 Spent Drilling Wastes Disposal and Treatment Technologies

1.7.1.1 Burial and Evaporation

Burial merely involves the placement and covering of spent drilling fluids into man-made excavations, such as pits or landfills or into natural excavations. Evaporation on the other hand involves the use of solar energy to evaporate the drilling fluid, the residue (predominantly cuttings) could either be hauled offsite or buried in the pit [20]. From available statistics for the time period within 1985-1995 onsite burial and evaporation was the most common onshore technique used for disposing drilling wastes, according to the report "two-thirds of the drilling wastes (68 percent) were disposed onsite through evaporation and burial" [11]. Table 1.1 is adopted from reference [11].

Table 1.1 Spent drilling waste disposal practices [11]

Comparison of 1985 and 1995 Drilling Waste Disposal Practices		
Drilling Waste Disposal Method	% Drilling Wastes 1985	% Drilling Wastes 1995
Evaporation On site	29	47
Hauled Offsite	28	2
Injection	13	13
Buried on Site	12	21
Discharge to Surface	10	1
Landspread	7	7
Others (Including solidification and incineration)	1	2
Total (%)	100	100

Onsite burial and evaporation is a low-cost, low-technology method. It does not involve waste hauling from the drill site thereby significantly reducing disposal costs making this technology a very attractive technology to most operators especially independent operators.

The burial could be done in the reserve pit or in a landfill depending on the site location, soil type, land topography and drilling fluid used; the pits may be lined to avoid leaching into the subsurface. This technology requires no special personnel training as long as issues such as soil type, chemical constituents of the drilling fluid are well characterized and issues such as leaching, soil and freshwater contamination have been already addressed in the drilling plan.

Limitations to this technology are numerous. This technology cannot be applied in areas with high permeability soils such as sands and are consigned to regions with clays. This technology requires a continuous degree of monitoring as the operator must ensure that the constituents of the pit do not leach into the subsurface as liability and clean-up costs are very prohibitive aside from the intangible costs of a damaged reputation. Evaporation is dependent on the sun. When drilling in seasons such as winter or in regions with low sunshine or during heavy rains it becomes unrealistic to evaporate the liquid part of the wastes which could increase in the event of heavy rainfall. Evaporation as a means of getting rid of the liquids could also introduce Volatile Organic Compounds (VOCs) into the atmosphere [21].

Burial of wastes creates anoxic conditions that do not facilitate favorably the biodegradation of majority of harmful compounds thereby posing a latent source of contamination. Burial into landfills evokes social concerns about sustainability as landfills are viewed as generally unsustainable despite improved lining technology over the years because landfill space is deemed correctly finite. As subsurface reach continues to increase as show in Figure 1.2, waste volumes would continue to increase. Assuming all factors favor burial and evaporation such as geological suitability, sunshine and infinite space, the footprint of using burial and evaporation technology shall offset any gains made at reducing footprint as impoundment sizes would increase commensurate to the volume of wastes produced.

Considering the advantages and limitations of on-site evaporation and its impact on the environment, this technology despite its huge cost advantage presents limitations that greatly outweigh it advantages. A larger footprint would be the outcome of this technology and this technology does very little in addressing the issues of re-use and or recycle of valuable non-toxic water resources that could be put to better use. Though the need for a reserve pit is well understood in the drilling process, the use of onsite burial based on environmental friendly principles makes this technique rate very low.

1.7.1.2 Land Application

Land application is a widely used treatment or disposal option in the industry. Various technical papers describe treating drilling wastes using land application particularly hydrocarbon contaminated drilling wastes and tank bottoms [22]. Land application involves the controlled application of wastes to the land. It employs the soils naturally occurring microbial populations to break down the hydrocarbons or contaminants transforming them to less harmful compounds (biodegradation) or preferably utilizing the contaminants breaking them down to carbon dioxide and water (mineralization).

Land application can be considered a waste treatment option or a waste disposal option or both depending on the intended use. Land application is generally divided into land farming and land spreading although the distinction between both groups is more gray than clear. Land farming generally refers to the repeated application of wastes to the soil surface whereas land spreading describes a onetime application of wastes to the soil surface, making the difference between both groups the frequency of application of the wastes. Both groups are lumped up as one in this discussion.

Land application thus involves the controlled one time addition and or repeated application of wastes to the soil surface employing microorganisms in the soil to biodegrade hydrocarbon constituents. Persistent contaminants, heavy metals and other xenophobes are transformed into less harmful compounds or completely mineralized during biodegradation. It is a relatively simple technique and requires more microbial and agricultural knowledge than engineering. This technology strives to create an enabling environment for microbial populations to biodegrade the hydrocarbons and contaminants. Knowledge of soil type, water capacity, weather, nutrients are essential for successful application of this technology while monitoring is essential to avoid anoxic conditions that would stymie biodegradation and create a hazard.

Land application is a relatively low-cost drilling waste management technique. It is best used in areas where there is an abundance of land. Land applications could be a very effective treatment technique because micro-organisms are very efficient degraders of hydrocarbons and various drilling wastes contaminants. Input into the system is minimal and degradation could be accelerated or optimized through the addition of fertilizers. Studies show that land farming does not adversely affect soils and may even benefit certain sandy soils by increasing their water-retaining capacity and reducing fertilizer losses [23]. Inorganic compounds and metals present in the drilling wastes are diluted in the soil, and may be incorporated into the matrix through chelation, exchange reactions, covalent bonding, or other processes reducing the availability of the contaminants [24].

Land application is limited by available land space and there is also the risk of groundwater contamination in areas with shallow water tables as there exists the risk of percolation or leaching of contaminants. Moderate to high salt concentrations in drilling wastes could be prohibitive to biodegradation and soil structure [24]. Moisture level control is also important in land applications as too much moisture creates waterlogged soils which are not conducive to biodegradation and too little moisture hinders metabolic activity of the micro-organisms thereby causing little or no biodegradation. Land application is not a quick process it may require long periods of time ranging from a few months to a few years to achieve biodegradation and or mineralization depending on the type of contaminants and volume of wastes to be treated. The larger the waste volume the larger the space required and the more recalcitrant the contaminant the longer the biodegradation/mineralization process.

With respect to EFD, land application as a technique poses some challenges with respect to footprint and recycle and re-use. Land application techniques increases the footprint of drilling operations and with increasing subsurface reach the amount of land needed for land applications would continue to increase due to the increasing volume of wastes. So unless there is a compaction of the waste to be treated there shall be a need for increased land space. Limitations are posed by the volume of waste that can be applied over the land causing space constraints apart from residence time on the land. Recycle and re-use gains are moderate as the land could be applied for other uses such as farming or allowed to fallow after treatment of the waste. This technology is rated moderate.

1.7.1.3 Bioremediation

Another disposal and or treatment technique also used in the disposal of E&P wastes is bioremediation. The underlying principle in bioremediation is the same as in land application i.e. employing micro-organisms to degrade recalcitrant compounds such as hydrocarbons. Bioremediation differs in practice to land application in that there is an intended objective to accelerate the biodegradation process by actively creating, controlling and managing parameters that affect the microbial biodegradation process, such as oxygen, nutrients, moisture content and pH.

There are basically two common bioremediation techniques in dealing with drilling wastes, composting and bioreactors and there is a third emerging technique –vermiculture or vermicomposting [25]. Though bioremediation is proven to be effective it faces wide adaptation constraints on a large scale in the oil and gas industry due to the large volumes of wastes generated in exploration and production activities. Impoundment size, energy and loading restrictions are common problems associated with adopting bioremediation aside from retention or residence time constraints, monitoring costs and additional personnel. The three different techniques shall be briefly described and assessed as to their limitations and how they fit into the environmentally friendly drilling concept.

1.7.1.3.1 Composting

During composting waste is mixed with bulking agent such as saw dust, straw or rice hulls and organic amendments such as animal or vegetative wastes, under controlled moisture and oxygen levels to attain degradation or transformation of contaminants. Bulking agents serve to increase porosity, reduce soil bulk density, oxygen diffusion and in some cases help to form water stable aggregates [26]. Organic amendments serve to shore up the nutrient base of the soil by enriching the soil enhancing microbial activities. The combination of the soil-waste-bulking agents-organic amendment is called the compost when mixed together and piled.

Nutrient ratio, waste loading, aeration and moisture level management are essential to successful composting as waterlogged composts without proper aeration create anoxic environments.

Composting is a very effective process in the treatment of drilling wastes as significant reduction of contaminants is achieved in less than two months in some cases (time varies depending on various factors such as contaminant loading)[27]. Compositing requires less land than land farming applications and can handle comparably higher oil content in the waste, initial oil concentration can be as high as 15-25% after bulking agents have been added [26,27,28]. Composting can also be used in cold regions [29] and to reasonable extent it can be used in inclement weather such as during rains as the compost piles may be covered. The end product of composting is of value as the compost can be used for purposes such as agriculture and various other uses where compost is needed.

Issues with composting lies in regular maintenance, the compost cannot be left to "fallow" as constant monitoring of the temperature, moisture level and pH is essential, lack of which could cause the compost failure and could be toxic in some cases. Aeration during composting could be forced or just by turning periodically the compost, this involves additional manpower or equipment when compared to land farming and this also increases the cost of composting in comparison to land farming.

In the light of EFD principles, composting as treatment or disposal technology has a low-medium footprint. There is also possible re-use of the compost after composting making it more environmentally friendly. The ease of adaptation of this technology is above average as many operators have used composting in treatment of drilling wastes with very encouraging results and large scale compost operations exist. As with land application higher waste volume generation can affect the long-term viability of using composting due to land constraints and the manpower and resources used in monitoring.

1.7.1.3.2 Vermicomposting

Application of vermicomposting to drilling waste is novel. Vermicomposting has a long but uncommon history in the degradation of organic wastes such as municipal waste and very few vermicomposting plants or projects are known. Vermicomposting involves using worms in the bioremediation of waste, these worms through their burrowing increase aeration, surface porosity and stabilize the compost increasing the microbial activities of the degrading microbes. The activities of the worms also reduce the monitoring required and when they die offer additional organic fuel to the microbes. Paulsen et al [25] were the first to report using vermicomposting on spent drilling fluids.

Their experiment carried out in Norway involved windrows similar to those in composting; they used wood bark and chipping as bulking agents while manure, worm cast and clay were the organic addendum to make the compost. The cuttings used by Paulsen et al were mineral oil contaminated drill cuttings. After approximately 70 days and about four loads of drill cuttings they reported a reduction in the oil content to background levels also showing heavy metals reduction to levels below the Norwegian regulatory limits. Advantages of composting apply to vermicomposting and vermicomposting might hold the additional advantage of requiring less monitoring as the parameters monitored in normal composting is “biologically monitored” in vermicomposting.

From the Paulsen et al study it might be surmised that vermicomposting might take up more land space than actual composting as windrows have vertical limitations in vermicomposting. Since literature is scant, comparing specifics between vermicomposting of drilling wastes and composting of drilling wastes is quite difficult. For Best Available Technique for drilling waste disposal and treatment especially for environmentally sensitive areas, vermicomposting scores very high though there are practical issues with its adaptation such as drilling waste composition, climatic conditions, volatilization issues and also the limited space rationale in the light of increasing subsurface reach of drilling operations.

1.7.1.3.3 Bioreactors

Bioreactors work on the same principle of bioremediation and land application – employing micro-organism for the break-down or transformation of the contaminants and hydrocarbons in the drilling waste the underlying difference is that biodegradation is carried out in either a closed or opened vessel. The vessel confers a higher degree of control of biodegradation parameters over other techniques that employ bioremediation and this degree of control is intended to optimize biodegradation. Due to this degree of control higher biodegradation rates are encountered in bioreactors than other techniques. In biodegradation micro-organisms could be seeded in the reactors with the drilling waste and stirred, aeration is achieved through intensive mechanical stirring and the major goal in the reactor is the increase of contact between the micro-organism and the contaminants.

The waste is introduced periodically into the system at the start, microbial growth time is allowed for proliferation of the microbes in the system and to allow adaptation of the microbes to the waste. Biodegradation parameters such as oxygen levels, pH, and temperature are monitored usually automatically and they serve to indicate efficiency of biodegradation. Bioreactors can operate in batch, semi-batch and continuous modes. Solids loading in the bioreactor on a dry weight basis is usually about 15 to 20 percent although special reactors can handle up to 40 percent [30]. The material which the reactor is made of or how it is protected is of importance due to the abrasive nature of the drilling solids when vigorously mixed. An obvious great advantage of the bioreactor is the ability to use it in any weather or climate condition and the faster biodegradation rates.

Pilot tests are very essential to the successful operation of bioreactors due to the complexities involved in maintaining the biodegradation parameters and reactor environment. Mcmillien and Gray [30] demonstrated the degradation in a bioreactor of mineral oil in oil-based drill cuttings that contained 15 percent oil and grease. The mineral oil was Escaid 110 which is a low molecular weight refined product consisting of normal and cyclic alkanes with less than one percent aromatics, the drill cuttings contained 58 percent solids and 3.5 percent calcium chloride. Using different solids rate in the pilot bioreactors over a 35 day period, they reported impressive reductions in the oil and grease content, using a 5, 15 and 25 percent solids loading they reported oil and grease reduction from about 10 percent to about 100 percent.

Limitations to bioreactors have to do with the sizes of the impoundment, loading rates and the characteristic of the waste and these factors are not mutually exclusive but interrelated. Drilling wastes vary from drilling location to drilling location and in order to use bioreactors for drilling waste treatment a more detailed knowledge of the waste is needed relative to other bioremediation methods. For example most waste can be composted or landfarmed but practical considerations limit what can be biodegraded using a bioreactor. In a bioreactor the aim is to increase contact between the micro-organisms and the waste, the contaminant is bound to the solids and adsorbed to the solids causing a theoretical and practical limitation on how much solids can be loaded on the system.

Since loading limitations cannot be ignored, a larger vessel is needed to increase contact and more freshwater would be needed to dilute the cuttings and more microbial population added. This would also bear on the power needed to mechanically stir the bioreactor constituent and energy needed for forced aeration. Ultimately the residence time of the waste in the bioreactor invariably would be affected and this would be a limiting factor in determining how much waste can be treated. These amongst many problems are issues with adaptation of bioreactors on-site for waste treatment of drilling wastes.

With respect to EFD, bioreactor treatment of drilling wastes is in theory a very environmentally friendly option with bioreactors. Land space is more optimized when compared to other options discussed above and we have the disappearance or transformation of the contaminant. Practical issues with the adaptation of bioreactors for field operations in the light of the volume of waste generated obviate the gains of being environmentally friendly, the use of large vessels and their energy requirements indirectly increase footprint. Impact due to volatilization of contaminants is also worthy of consideration though emissions could be controlled by using control devices such as activated carbon filters to the gas exhaust steam of an enclosed bioreactor [30]. Another indirect issue with bioreactors remain that due to the addition of copious amounts of freshwater the waste volume is increased and when the biodegradation occurs the treated water is still present. So except the operator is allowed to dump the waste, additional costs would be needed to truck the waste to a disposal facility dumping also reduces the ability to re-use the waste.

1.7.2 Produced Water Treatment or Disposal

1.7.2.1 Subsurface Injection

Subsurface injection in the disposal of produced water is a very common disposal option in the oil and gas industry. Subsurface injection is also used for disposal of drill cuttings (slurry made up of drill cuttings) and produced water. Subsurface injection is very common in produced water disposal and the type of subsurface injection used in waste disposal depends on the location of the wastes and injection location. The growing position of subsurface injection and its role as the major disposal option of produced water cannot be understated and is the major highlight of this section. The discussion starts off describing slurry injection and narrows the discussion to produced water disposal.

Injection is recorded to have begun in the mid-1980 with small volume annulus injection in the Gulf of Mexico [31]. It began to gain broader use in various regions; operators started to use it in Alaska, the North Sea and in limited regions of South America and by the end of the mid 1990's commercial facilities with dedicated injection wells began operation [32]. This was followed by large scale injection operations in Alaska and the Gulf of Mexico [33,34] and today the use of injections as a disposal technology is quite commonplace and increasing. In slurry injection "the two most common sources of waste injected are from on-going drilling operations and from mud cuttings that have been temporarily stockpiled pending some future permanent disposition. Cuttings from an on-going drilling operation are usually retrieved from the shale shaker, mixed with water, processed to an appropriate size and injected downhole" [35].

1.7.2.2 Slurry Injection

There are two common types of slurry injection or two typical wellbore configurations for slurry injection, annulus injection and disposal well injection, these two configurations are shown in figure 1.4.

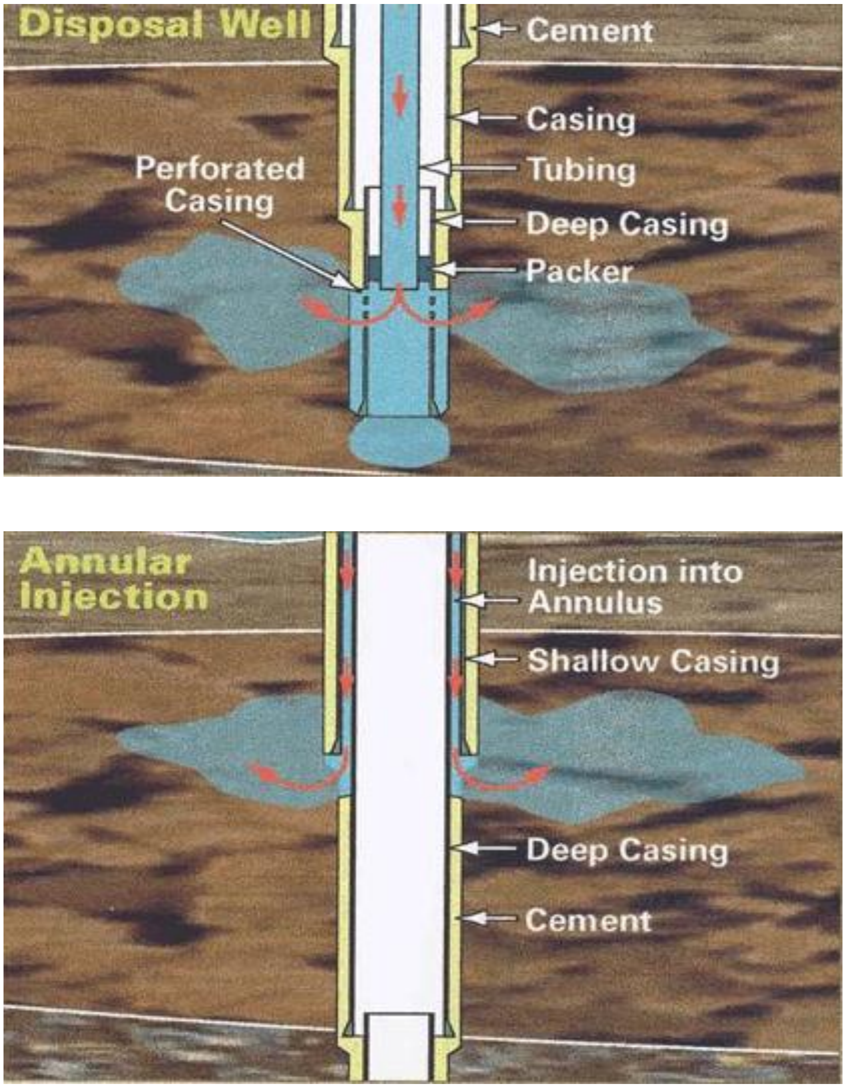


Fig. 1. 4 Schematic of Injection. Top: Disposal well injection. Below: Annular injection [24].

In annulus injection the waste slurry is injected down the annulus (the annulus refers to the space between the two casing strings) between the surface casing and a deeper casing string so the waste slurry enters the formation at the lower end of the deeper casing string. Annulus injection is more common offshore where the cuttings are injected into either the uphole annulus of the well being drilled or into the annulus of the nearby well. Injection rates are typically about 1 to 6 barrels per minute (BPM) and the duration of injection into the annulus is about the drilling time with total slurry volumes injected usually between 10000 – 50000 barrels per well [35].

The second configuration of slurry injection, injection into a disposal well is more typical of longer-term, permanent injection operation. It involves injection to either a section of the drilled hole that is below all casing strings, or to a section of the casing that has been perforated with a series of holes at the depth of an injection formation [24]. In some instances existing producing wells are recompleted as injection wells while in some other instances dedicated injection wells are created and usually the latter wells are functional for long periods of time and can have slurry volumes of about 2 million barrels per well [35]. Injection into disposal wells has typical injection rates of about 5 and 25 barrels per minute (BPM), significantly higher than annular injection primarily due to the tubing having lower friction losses compared to the losses down an annulus.

Implementing the slurry injection involves identification, collection and transportation of solid waste for slurrification. The particles are made relatively homogenous by grinding; a mean particle size of about 300 microns is believed to be about appropriate [36]. This particle size is essential to avoid “bridging and plugging of either the re-injection annulus or disposal fracture in the well region” [36]. The slurry is then transferred to a slurry holding tank to condition the slurry rheology, it is then pumped into subsurface fractures which arise by injecting the slurry under high pressure into the disposal formation. This injection is usually done in batches as this allows the disposal fracture to close unto the cuttings and redistribute any pressure build-up in the formation. Figure 1.5 shows a schematic of drill cutting slurry fabrication and injection system (adapted from [36]). Freshwater or brine is used in the slurry preparation.

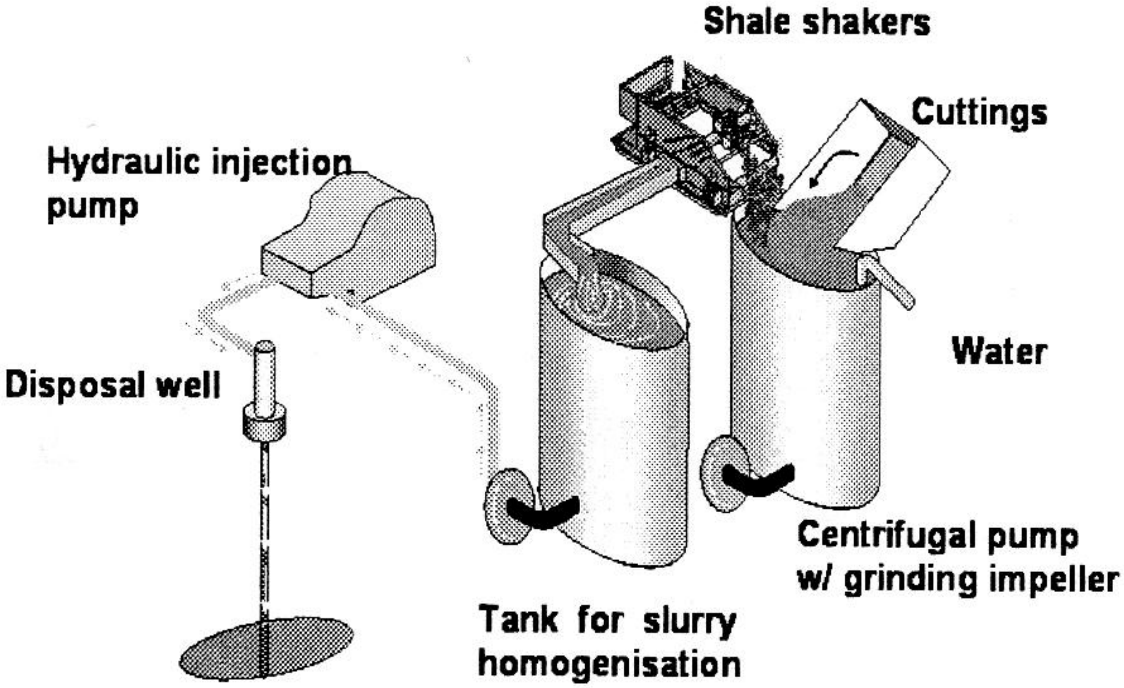


Fig. 1. 5 Schematic of drill cuttings slurry fabrication and injection system [36].

1.7.2.3 Produced Water Injection

Slurry injection pertains mainly to drilling wastes that are predominantly solid in nature (though not excusive), in the disposal of produced water significant amount of produced water is disposed using injection wells usually after de-oxygenation of the produced water. The EPA regulates the injection of produced water using the Underground Injection Control (UIC) regulation and the wells used for injecting produced water are described as Class II injection wells. Wells dedicated to disposal of produced water are termed Class II-D wells because apart from disposal of produced water, produced water is also used for enhanced recovery operations where they are injected into a producing formation to help move crude oil to wells for collection. This stimulation method is generally termed water flooding, and it is designed to increase the yield and productive life of usually mature oil deposits. Recovery wells of this nature are termed class II-R injection wells.

Produced water injection into Class II-D is also similar to slurry injection as it aims to ensure the containment and confinement of the injected water within acceptable injection zones away from any underground source of useable water for drinking or irrigation [37]. Produced water injection could either be by fracture injection (similar to slurry injection explained above) or matrix injection. Matrix injection involves the deposition of the contaminants into the pore spaces of the rock without actually fracturing the formation [37]. Matrix injection involves allowing the contaminant (solid and oil-in-water) deposition and formation plugging to occur in a limited area around the injection well, substantial pilot knowledge and reservoir pressure history is needed to successfully implement a matrix injection.

Injection of wastes has a lot of advantages to operators in the industry as it helps them achieve zero discharge of waste i.e. there are no waste left after the completion of the drilling operation. It also saves on transportation and associated costs as injections are usually done in areas close to or where the waste is generated and If there are no issues with the well integrity there are no clean-up liabilities. The economics of scale makes it economically favorable to inject, from one study for a 20-well program in the Gyda/Ula field in the North Slope, the economic analysis showed that injection costs would be approximately 10 million dollars compared to 18 million dollars for onshore processing [38].

Disadvantages to the use of injection as a disposal primarily revolves around well integrity. The ability to inject depends on the subsurface geology of the formation receiving the waste along with its compatibility to the chemical and physical characteristics of the waste. The protection of groundwater aquifer from contamination is an overriding concern and this has informed increasingly stringent permitting and regulation hurdles which are expected to be more stringent in the coming years. Well failures do occur though they are not very common, for example "excessive erosion wear from long-term slurry injection has caused well integrity failures both in the Gulf of Mexico and in the North Sea operations" [35]. Well integrity issues arising from poor slurry rheology design, overburdening beyond the well capacity, poor monitoring and poor procedures present a large potential for liability for operators.

With respect to Environmentally Friendly Drilling, injection of wastes is not a viable option in fragile ecosystems as regulatory agencies and community stakeholders would balk at the prospect of any breach of the well's integrity. The footprint of equipment needed in the injection such as hydrocylones, centrifuges, crushers, air flotation equipment e.t.c. all add considerable footprint to drilling operations. With respect to footprint on the surface, when compared to other treatment methods injection moderately compares as a small footprint after processing the waste for injection.

With regard to recycle or re-use there is little or no re-use especially in produced water injection (it should be noted that injection for enhanced recover would fall under re-use, the wells referred to in this section are Class II-D wells). The large volumes of produced water disposed represents a huge source of freshwater if desalinated or a large source of water for re-use especially for re-uses in oil and gas operations. Possible re-use of injected wastes for drilling or associated operations would go a long way in greatly reducing the pressure for freshwater for oil and gas operations. Due to greater subsurface reach disposal or treatment options must look towards re-use and recycle to reduce the amount of water resources being disposed. Though the footprint of injection might seem small on the surface, the re-use and recycle level is dismal in the light of the potential for water conservation it poses. Produced water injection remains the prominent disposal option in produced water management and disposal, though other disposal options exists such as thermal treatment they currently pale in comparison to scale and use of produced water injection.

1.8 Technologies Summary

Present disposal and or treatment technologies have shortfalls when the concept of environmentally friendly drilling is used to appraise them, some shortfalls arise because of the need to see land as finite and the need to minimize footprint irrespective of land available.

Shortfalls such as low re-use and recycle bedevil technologies that seem to have low footprints and some effective treatment methods are just transference of the contaminant to a different media. The real life adoption of these various technologies are governed by various factors such as cost, existing regulations in areas of operation, public perception, stakeholder involvement, existing technology, adaptability of the existing technology and the cost benefit-ratio.

There are associated issues also with increased waste generation, one being that larger waste volumes due to greater subsurface reach is limiting waste treatment or disposal options. The traditional waste treatment options such as land application, bioremediation, bioreactors, incineration and a host of other treatment options are increasingly becoming uneconomical because of the large volume of wastes to be treated. It is becoming self-evident that treatment technologies aimed at treating drilling waste that are beneficial to the environment are made impractical due to the volume of waste generated. Earlier in this research a preliminary investigation was carried out looking at what it would take to treat drilling wastes using bioreactors, it was concluded that due to the volume of waste generated in drilling operations and assuming above normal improved theoretical biodegradation rates and residence time, bioreactors were simply impractical.

Regulations and liability issues are increasingly making land application technologies obsolete as regulatory bodies are making stricter laws concerning land application as a treatment option to protect groundwater and soil contamination [17]. Public perception is increasingly against disposal or treatment technologies that pose a threat to the environment despite safeguards by operators; these concerns helped accelerate slurry and produced water injection as the most favored disposal technology presently [35]. Injections are seen as the next conducive option because much safer technologies have been impractical to waste volumes and waste composition. Though operators recognize the need for environmentally friendly treatment/disposal technologies as the future, practical issues with the present or upcoming alternatives make them hard to adopt despite good intentions.

Associated issues such as energy demand accelerating the exploitation of unconventional create unique problems with freshwater sourcing and waste disposal forcing a paradigm shift about water use. Considering a conservative estimate of 390 million gallons of produced water injected daily into injection disposal wells [39], the historical daily average use of water in college station as of 2006 is 12 million gallons per day and the United States Geological Survey estimates that the average American uses between 80 - 100 gallons of water per day. Thus the amount of produced water injected daily is approximately the daily water need of about 4 million Americans and 35 times the city of College Station daily use! Though slurry and produced water injection have the semblance of “disappearing waste” present reality dictates that freshwater sourcing could easily become a limitation factor in the exploration and production of oil and gas as operators are increasingly putting pressure on freshwater sources to meet increased E&P needs.

In summary the need for technology that tackles the increasing waste volumes as a result of increasing subsurface reach achieving volume reduction of the waste and at the same time actively increasing the options of recycle and re-use is pressing. This technology would help reduce waste disposal costs by reducing hauling costs through volume reduction and treatment costs. Volume reduction would also reduce the footprint of drilling operations by reducing the size of impoundments needed, allowing for drilling in sensitive ecosystems by significantly reducing the impact of increased wastes. Social gains and positive perception would be sure to follow such concrete steps at environmental stewardship.

Two central issues have been identified; one, that the impact of drilling operations on the environment is bound to increase due to increased subsurface reach as more waste is produced and the footprint of drilling operations increases though rig sizes are reducing. Second, that there exists large volumes of recoverable or re-useable wastes that are disposed off with minimal re-use, especially produced water. In the face of increasing populations and the threat to freshwater sources coupled with environmental concerns there is a need for better stewardship in disposing water based E&P wastes. Associated issues that revolve around these two central issues include the reduced likelihood of permission to exploit the O&G resources in areas deemed sensitive to the public by regulatory agencies, reduction in alternative treatment options due to increased volume of wastes and the increasing associated costs with disposal options and issues with hauling over long distances.

1.9 Membranes

1.9.1 Introduction

Membranes are semi-permeable materials that are used in the separation of particles ranging from bacteria to atoms [40,41]. Membranes acts primarily as a selective barrier in the presence of a driving force allowing the passage of particular particles/components of the stream based usually on size (filtration) and the retention of anything larger. Membranes inadvertently act to enrich one of the streams (permeating or retaining) in one or more constituents. Separation by membranes is not confined to particle separation but extends filtration to include the separation of dissolved solutes in liquid streams and separation of gas mixtures [40]. In membrane terminology the permeate is that part of feed solution that passes through the membrane, while the retentate is that that part of the feed solution that is retained on the side of the membrane.

The driving forces in membranes could either be chemical potential as seen in osmosis, concentration difference as seen in dialysis, voltage or current as seen in electrodialysis or pressure as seen in microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). The membrane processes considered in this thesis are limited to pressure driven processes where the driving force is a pressure difference across the membrane. Pressure driven processes are by far the most common processes and probably the most investigated processes as they find wide use in various industries and in various processes. This being said membranes in general find wide application and serve wide purposes from the pharmaceutical industry to the space industry.

Membranes can be active or passive in the filtration process, according to Cheryan[40] “membranes can also physically or chemically modify the permeating species, conduct electric current, prevent permeation or regulate the rate of permeation (as in controlled release technology). So membranes may either be passive or reactive depending on the membranes ability to alter the chemical nature of the permeating species” [40]. Depending on the type of membrane used and the nature of the driving force significant changes can be made to the product (either the permeate or the retentate depending on the need) and this mandates the investigation into membrane processes and membranes before application to a process.

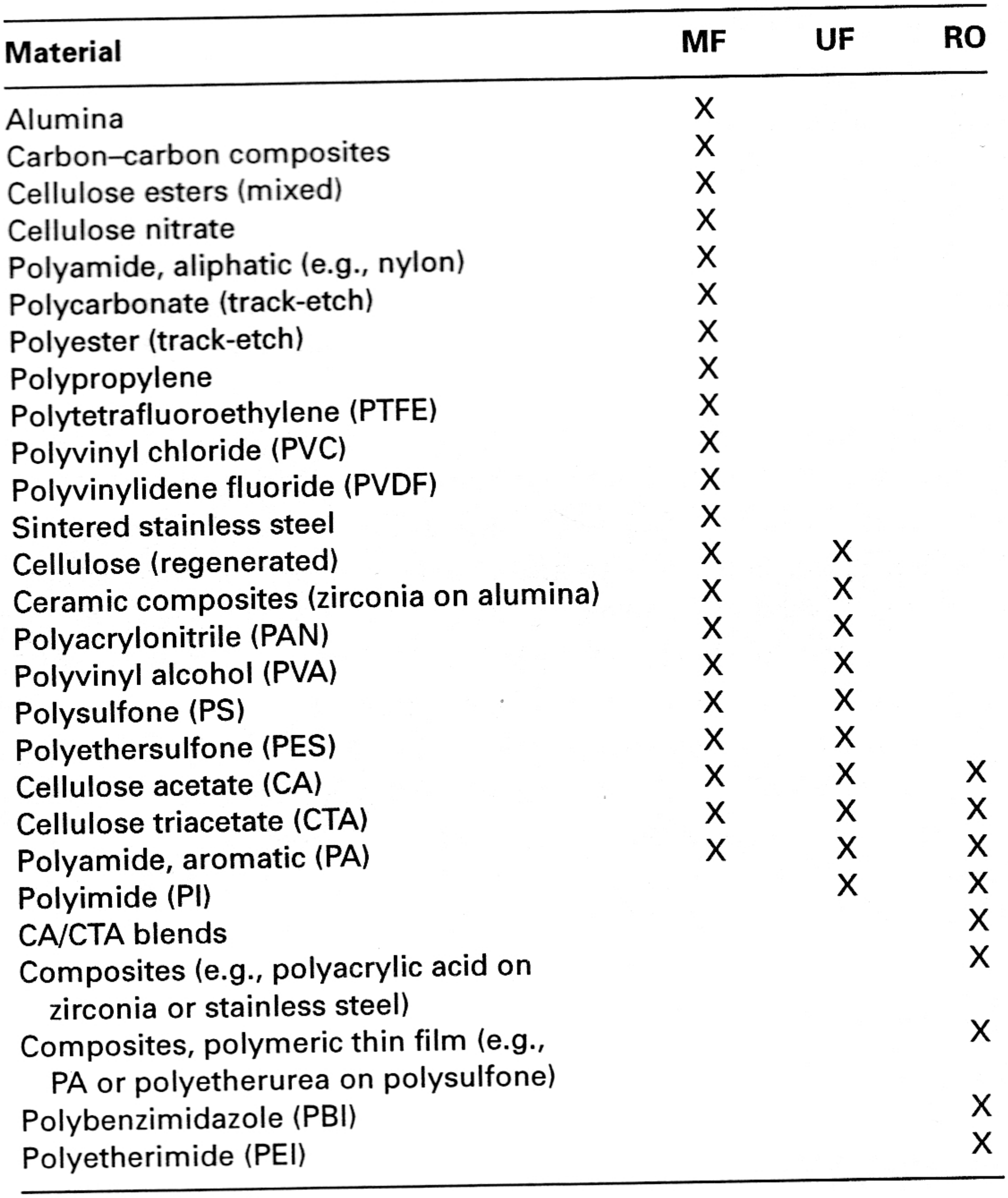
1.9.2 Classification

There are varied membrane classifications. Some are based on the application of the membrane; gas-liquids, liquid-liquids, solids-liquids separations, some are based on the nature of the constituent material the membrane is made from – natural or synthetic, some are based on the mechanism which the membrane achieves separation –ion-exchange, osmotic, adsorptive or diffusive e.t.c. and some classifications are based on the structure of the membrane i.e. porous or non-porous [42]. Due to these varied classifications there are multiple conflicting terminologies and varied membrane descriptions. Three classifications of membranes pertinent to this thesis shall be used, classifications based on membrane materials, classification based on the various pressure driven membrane processes and the classification based on membrane modules.

1.9.2.1 Membrane Materials

Various materials have been used in membrane manufacture, literature surveys of known membrane materials indicates that there are over 130 different materials used in membrane manufacture, though only few have gained commercial status or approval for use in various industrial processes [40]. Table 1.2 shows a few materials used in the membrane manufacture of pressure drive processes, a few of which shall be described here, this description should not been seen as exhaustive of membranes materials rather a highlight of some membranes materials.

Table 1.2 Some membrane materials [40]



Material	MF	UF	RO
Alumina	X		
Carbon–carbon composites	X		
Cellulose esters (mixed)	X		
Cellulose nitrate	X		
Polyamide, aliphatic (e.g., nylon)	X		
Polycarbonate (track-etch)	X		
Polyester (track-etch)	X		
Polypropylene	X		
Polytetrafluoroethylene (PTFE)	X		
Polyvinyl chloride (PVC)	X		
Polyvinylidene fluoride (PVDF)	X		
Sintered stainless steel	X		
Cellulose (regenerated)	X	X	
Ceramic composites (zirconia on alumina)	X	X	
Polyacrylonitrile (PAN)	X	X	
Polyvinyl alcohol (PVA)	X	X	
Polysulfone (PS)	X	X	
Polyethersulfone (PES)	X	X	
Cellulose acetate (CA)	X	X	X
Cellulose triacetate (CTA)	X	X	X
Polyamide, aromatic (PA)	X	X	X
Polyimide (PI)		X	X
CA/CTA blends			X
Composites (e.g., polyacrylic acid on zirconia or stainless steel)			X
Composites, polymeric thin film (e.g., PA or polyetherurea on polysulfone)			X
Polybenzimidazole (PBI)			X
Polyetherimide (PEI)			X

1.9.2.1.1 Polymeric Membranes

Cellulose acetate is a common membrane material used at the onset of modern membrane technology [43]. Cellulose is a polymer of β-1,4 linked glucose units with one primary and two secondary hydroxyl groups and the β- glucosidic oxygen in the equatorial position. Cellulose is derived from cotton linters or wood pulp and in some cases chemically modified wood pulp. To get cellulose acetate, the cellulose goes through acetylation which is a reaction with acetic anhydride, acetic acid and sulfuric acid to give the cellulose acetate. An important physical property that affects membrane properties and filtration is the degree of polymerization of the cellulose, the optimum appears to be 100-200 or 100-300 which would result in molecular weights of about 25,000-80,000 [41]. Cellulose acetate membranes are widely used for reverse osmosis and ultrafiltration applications [44], they have high hydrophilicity which is essential in minimizing membrane fouling, low production and manufacture cost and they can be produced with a wide range of pore sizes. Disadvantages are narrow temperature and pH ranges, low chemical resistance and they are highly biodegradable [42].

In order to address the short comings of cellulose acetate membranes other polymeric materials where created substituting various classes of materials in the polymer to address the shortcomings such as seen in polyamide membranes. Polyamide membranes have an amide bond in their structure (-CONH-) and were first made by DuPont, polyamide membranes have better resistance to hydrolysis and biological attack than cellulosic membranes and can be operated over a pH range of about 4 to 11. They also have better salt and water soluble organic rejection than cellulosic membranes and can withstand higher temperatures [45].Their shortcomings include low chlorine tolerance, biological fouling and compaction at high pressures and temperatures.

Polysulfone membranes are characterized by having in their structure “diphenylene sulfone repeating units. The –SO2 group in the polymeric sulfone is quite stable because of the electron attraction of resonating electrons between adjacent aromatic groups” [40]. Polysulfone membranes and polyethersulfone membranes are marked improvements over the cellulosic membranes and the polyamide membranes. They have wider temperature limits, wider pH tolerance with considerably better chlorine tolerance and are also easy to fabricate and manufacture [43]. Notable membrane polymeric materials that have excellent properties such as the polysulfone membranes include polyvinylidene fluoride (PVDF), polyetrafluororthylene (PTFE), polypropylene (PP), polystyrene (PS) and polyvinyl chloride (PVC), polyolefin (P) just mentioning a few. These materials confer on the membrane unique characteristics and additional tolerance to exacting operating conditions [46].

1.9.2.1.2 Inorganic Membranes

Inorganic membranes also called ceramic membranes spearheaded the latest revolution in membrane technology starting from the 80s [47]. Ceramic membranes are made from a wide range of inorganic materials and the more common ones are made from alumina, titania, zirconia and silicon oxides. In their manufacture they are often formed into asymmetric, multi-channel elements and normally have an asymmetrical structure composed of at least two, mostly three, different porosity levels. They are a vast improvement both in material characteristics and in the technology dividend to membrane filtration over polymeric membranes. They are inert to common chemicals and solvents, can withstand high acidity and alkalinity, have wide temperature, pH, and pressure limits, and their long life and durability increasing their appeal significantly. Limitations common to them include brittleness, relatively large energy consumption in running them (explanation is given in membrane module) and pore size limitation in the lower micron range.

1.9.2.2 Pressure Driven Processes

Another description that is of importance to this research are pressure driven membrane processes. There are four pressure driven membrane processes namely - microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). The underlying differences within these pressure driven processes is the different amount of pressure applied to achieve the separation and the size of the separation material; these combined factors determine the retentate and permeate characteristics. Table 1.3 shows the pressure- driven membrane processes and their separation characteristics.

Table 1.3 Pressure driven membrane processes [48]

Process Technology	Separation Principle	Size Range	MWCO	Objective
MF	Size	0.05 – 10 µm	-	Removal of suspended solids, bacteria, cysts and spores e.t.c.
UF	Size, Charge	1-50 nm	> 1000	Removal of both large dissolved solute molecules and suspended colloidal particles including protein, viruses e.t.c.
NF	Size, Charge, Affinity	~ 1 nm	200-1000	Removal of multivalent ions and certain charged or polar molecules such as sugars, pesticides e.t.c.
RO	Size, Charge, Affinity	<1 nm	<200	Removal of inorganic ions, salts and sugars

Reverse Osmosis is the tightest of the membrane types and it retains all components of the feed sample except the solvent (usually water), reverse osmosis is usually used to separate aqueous salts and ions with a molecular weight less than 200 [48]. Reverse osmosis membranes would reject high molecular weight compounds, low molecular weight compounds, glucose, amino acids and a host of different organics. Reverse osmosis finds wide application in different industries and processes, most common of which is desalination where reverse osmosis membranes are used to reduce dissolved solids from feed waters with salinities up to 45,000 ppm TDS (total dissolved solids). Compared to other pressure driven processes reverse osmosis is a high pressure process as the pressure applied is in excess of the osmotic pressure of the dissolved constituents to allow for flow of the permeate across the membrane. Reverse osmosis systems always have operating pressures of between 15-150 bar (217.5-2175 psi).

Nanofiltration is the next tight membrane type following reverse osmosis membranes. It uses charged membranes with pores that are bigger than reverse osmosis membranes but too small to allow the permeation of many organic compounds such as sugars [40]. It would reject high molecular weight compounds, monosaccharides, disaccharides and oligosaccharides , polyvalent negative ions and bigger molecules. It finds wide use in color removal, sugar and dye removal and removing THM precursors and hardness or sulfate from water. It has a pressure rating of between 5-35 bar (72.5 – 507.6 psi) and its mean pore size is also usually rated below 0.003 microns.

Ultrafiltration is the next tight membrane type following nanofiltration. Ultrafiltration is used in the separation of particles in the 0.02-0.2 um range. It finds common use in the retention of macromolecules such as proteins, polysaccharides, viral particles and some pathogens. It is a low pressure membrane system, ultrafiltration systems are rated for pressure between 1-10 bar (14.6 -146 psi). It has wide application in various industries and processes ranging from pharmaceutical, to food and beverage, agricultural and petrochemical processes. Ultrafiltration would be one of the membrane processes that shall be examined in this thesis for the filtration of water based E&P wastes.

Microfiltration on the other hand is the least restrictive pressure drive membrane process. It is used to separate particles in the micron range conventionally between 0.02 – 4 um, it removes bacteria, pigment, clay, suspended particles and larger sized solutes. It is also a low rated pressure process, microfiltration processes are rated for pressure less than 2 bar (29.2 psi). More membrane materials are used in microfiltration than any of the other pressure driven process and microfiltration finds wide use in various industries and processes. Though the delineation of the pore size range in each membrane classification seems clear theoretically, in reality this is not the case as there are usually overlaps in their classifications in different literature and from different membrane manufacturers. The pore size and pressure rating delineation vary from author to author, what is of importance is the graduation in rejection and added pressure as one goes from pressure driven process to another.

1.9.3 Membrane Module

Finally also of importance to this research is the membrane classification based on the module configuration. There are four recognized or common membrane modules [49]; the plate and frame, spiral wound, hollow fibre and tubular membrane modules. These modules can be built with various membrane materials and they are built for various purposes based on the intended need. No single module is deemed best but thorough knowledge of the feed stream to be treated, the economic and operational constraints and membrane filtration characteristics the choice of the most suitable membrane module for an intended purpose is arrived at.

1.9.3.1 Plate and Frame

Plate and frame type membranes are amongst the earliest membrane module type. It consists of a rigid, flat plate on which a flat sheet of membrane is placed and a spacer is put between the membrane and the flat plate. The spacer a netlike material is placed between the membrane sheets and provides channel for permeate flow and this sheet is sealed around the edges with a passage for permeate collection. This “unit” (membrane-spacer-membrane) is then stacked on top of each other or adjacent to one another depending on the decided orientation of the stack. The operation of the plate and frame module involves passing the feed through the plates and the permeate flows though spacer to the collection tube, the retentate goes through the module to the exit. See figure 1.6.

Advantages of the plate and frame include the ability for easy maintenance of the membrane module as replacement of the stack is easy and the cleaning equally easier and straightforward. In comparison to other modules based on cost of the material and module, the plate and frame module is cheap. The plate and frame module have intermediate energy consumption and packing density when compared against the spectrum of the tubular and spiral wound modules [50]. This module cannot handle high solids feed streams as the passage of the spacers would be easily blocked and are best adapted for low solids streams. Plate and frame modules find wide application in food and beverage industries and some chemical process lines.

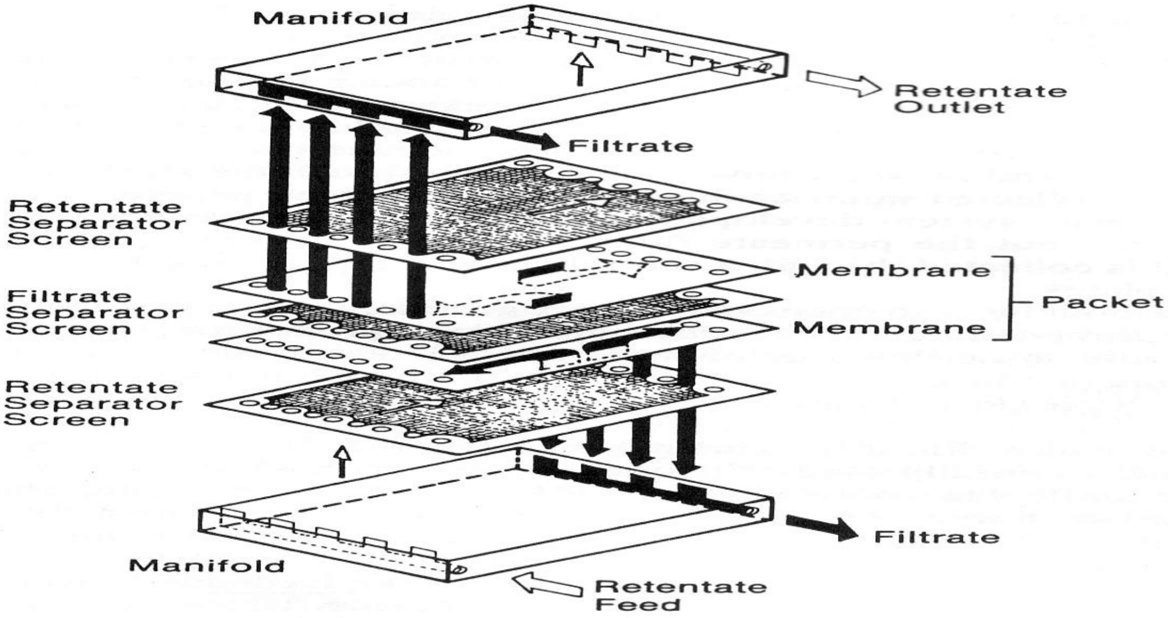


Fig. 1. 6 Schematic of a plate and frame membrane [42].

1.9.3.2 Spiral Wound Membranes

Spiral wound membranes are similar conceptually to the plate and frame module but differ in that the successive layers of membrane are wound around a perforated center tube. They are also designed around two flats sheets, with active sides (filtering sides) positioned opposite each other and separated by the same netlike spacer as in the plate and frame module, glued on the sides. Different from the plate and frame is that another spacer, the feed channel spacer, is placed on “one side of the envelope and the whole assembly rolled around the center tube in a spiral or jelly-roll configuration” [40]. The spiral wound is operated by pumping through the cross section on the module and the spacer channels permeate to the perforated tube in the center for collection. See figure 1.7.

Spiral wound membranes are famed to be the most compressed and economical design of membrane modules available commercially. Spiral wound membranes have the highest membrane area packed into a given pressure vessel with their surface to volume ratio averaging 200-300 ft^2/ft^3 [41,50]. They are reasonably priced and they are seen as membrane workhouses as they find wide applications in different industries, processes and systems. They also have low energy consumption and their capital costs are the lowest amongst most module designs. Their major limitations is similar to the plate and frame module as they cannot handle high solids feed without adequate pre-treatment as suspended particles are sure to block the channels created by the spacers.

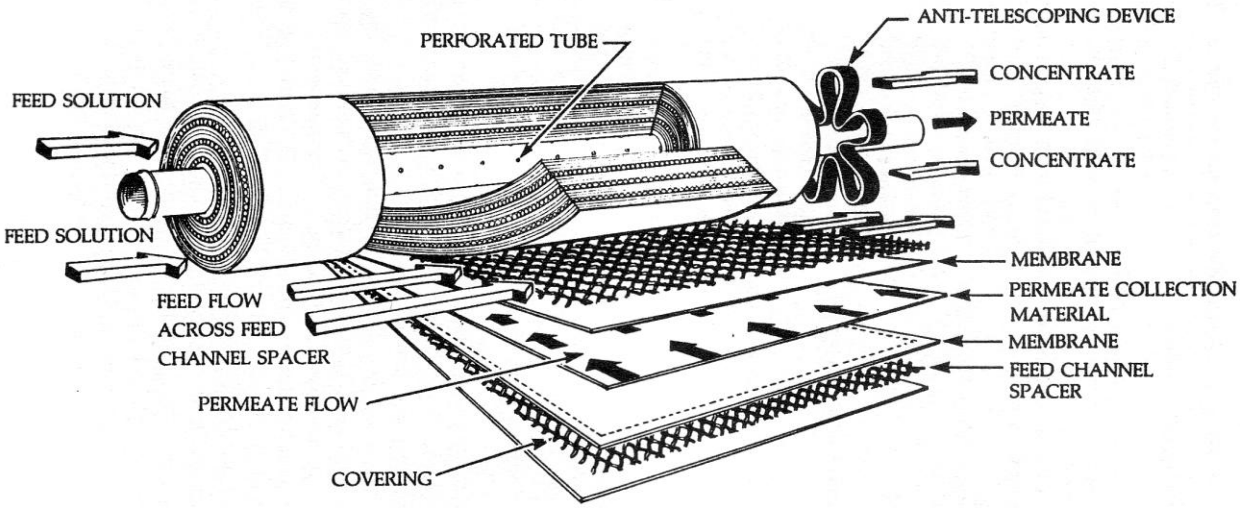


Fig. 1. 7 Schematic of a spiral wound [40].

1.9.3.3 Hollow Fiber

Hollow fibre membranes are basically made up of “spaghetti” like fibers bundled together and sealed by an epoxy resin plug encased in PVC, or acrylic tube or a fibre plastic. They are similar to the tubular membranes (discussed next) differing only in the fact that they stand alone (hollow fibre) and their internal diameter is less than 2 mm. They represent the latest of all membrane modules and have a high surface to volume ratio. They are made in a wide array of diameters from 100 micron to about 2 mm, “their fibers have a cross-sectional thickness of about 100 -400 microns with bundles containing about 50 - 3000 individual fibers sealed into hydraulically symmetrical housings in a shell-and tube arrangement bonded by epoxy at their end” [41]. See figure 1.8.

Advantages of the hollow fibre membrane include a high surface area to volume ratio, they have very low pressure rating with their maximum pressures hovering around 1.8 bar (25 psig), and also their energy consumption is relatively low when compared to other membrane modules. They have good backwash or back flush capacity and hollow fibre systems are usually built to carry out periodic backwash during operation such as seen in the Zenon 300 Unit built by GE. They can also handle moderate solids feeds though the flux would be higher if it had low solids. Disadvantages of the hollow fibre membrane are plugging of the small tube diameter, which could be addressed with an aggressive back flush regimen.

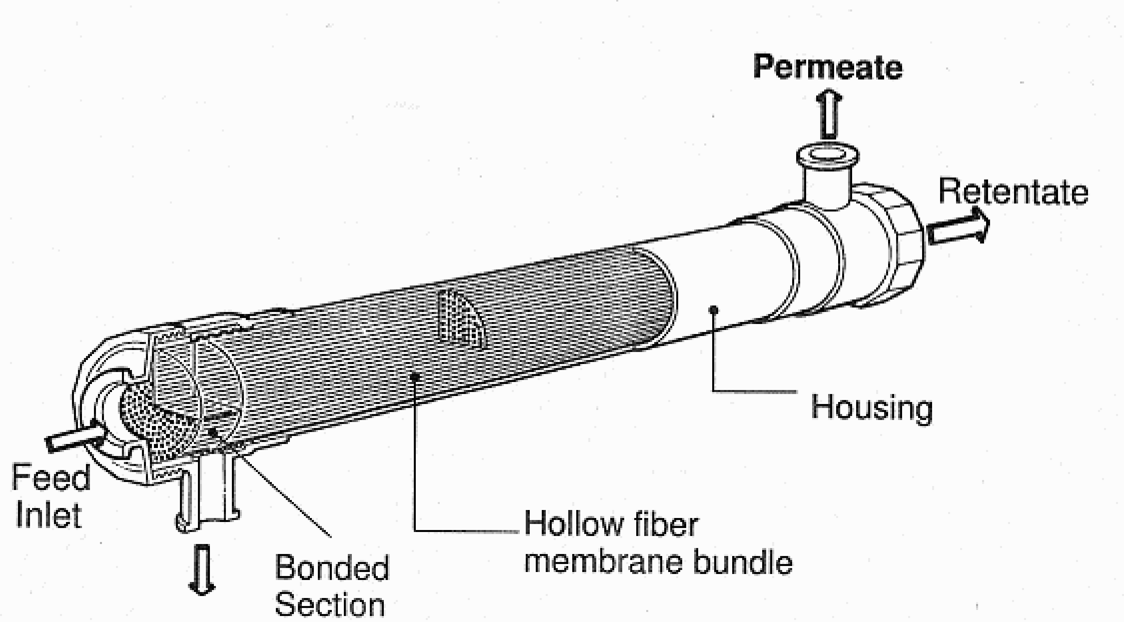


Fig. 1. 8 Schematic of a hollow fibre membrane [40].

1.9.3.4 Tubular Modules

Tubular membranes have the largest diameter of all membrane module types with internal diameters ranging from 0.5 – 1 inch (12.5 – 25mm) with lengths varying from the 2 to 20 ft (0.6 – 6.4m). As explained they differ from hollow fiber membranes in that they are supported along its length and cannot stand alone. Tubular membranes generally operate with the flow going through the internal diameter or lumen of the membranes and the permeate flowing outward from the skin of the membrane collecting in the housing where the membrane in fitted to a permeate collection outlet. Tubular membranes have low membrane densities, and a high flow demand when compared to other modules. See figure 1.9.

Tubular membranes are known to handle high solids feed more than any other membrane module type. They are also easily cleaned and have excellent backwash or back flush capacity like the hollow fibre, thus their tendency to fouling is lowest amongst the membrane modules. They have the lowest surface to volume ratio of all membrane modules and require more energy in their operation due to the high recirculation rates during operation. They are also relatively expensive as ceramic, polymeric and other tubular membrane modules cost more than other modules of the same material. Tubular membranes find wide application in a host of challenging rheological feed streams usually those with high suspended solids or with challenging chemicals such as solvents.

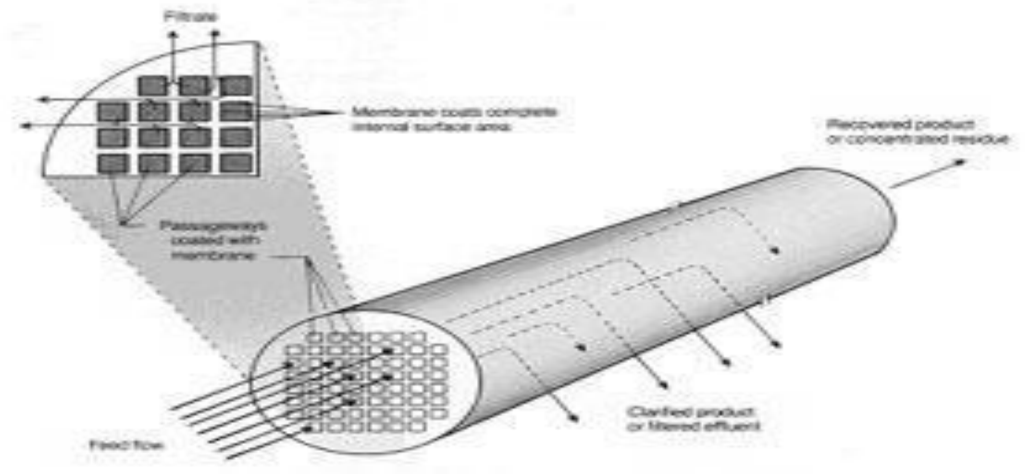


Fig. 1. 9 Schematic of a ceramic membrane.

1.9.4 Membrane Operation

There are two operating modes for membranes, the dead end filtration mode and the crossflow filtration mode. In the dead end mode the feed stream is pumped directly through the membrane. Figure 1.10a depicts the feed going into the membrane and one stream the permeate leaving the membrane. During dead-end filtration all the solvent that enters the membrane surface passes through the membrane while the solid particles or retentate stay behind on the membrane. Inevitably the solvent will experience greater flow resistance as the retentate builds up on the surface of the membrane resulting in flux decrease. Dead end filtration is common in low solids feed such as cartridge filtration of boiler feed or ultrafiltration of apyrogenic pure water production [48].

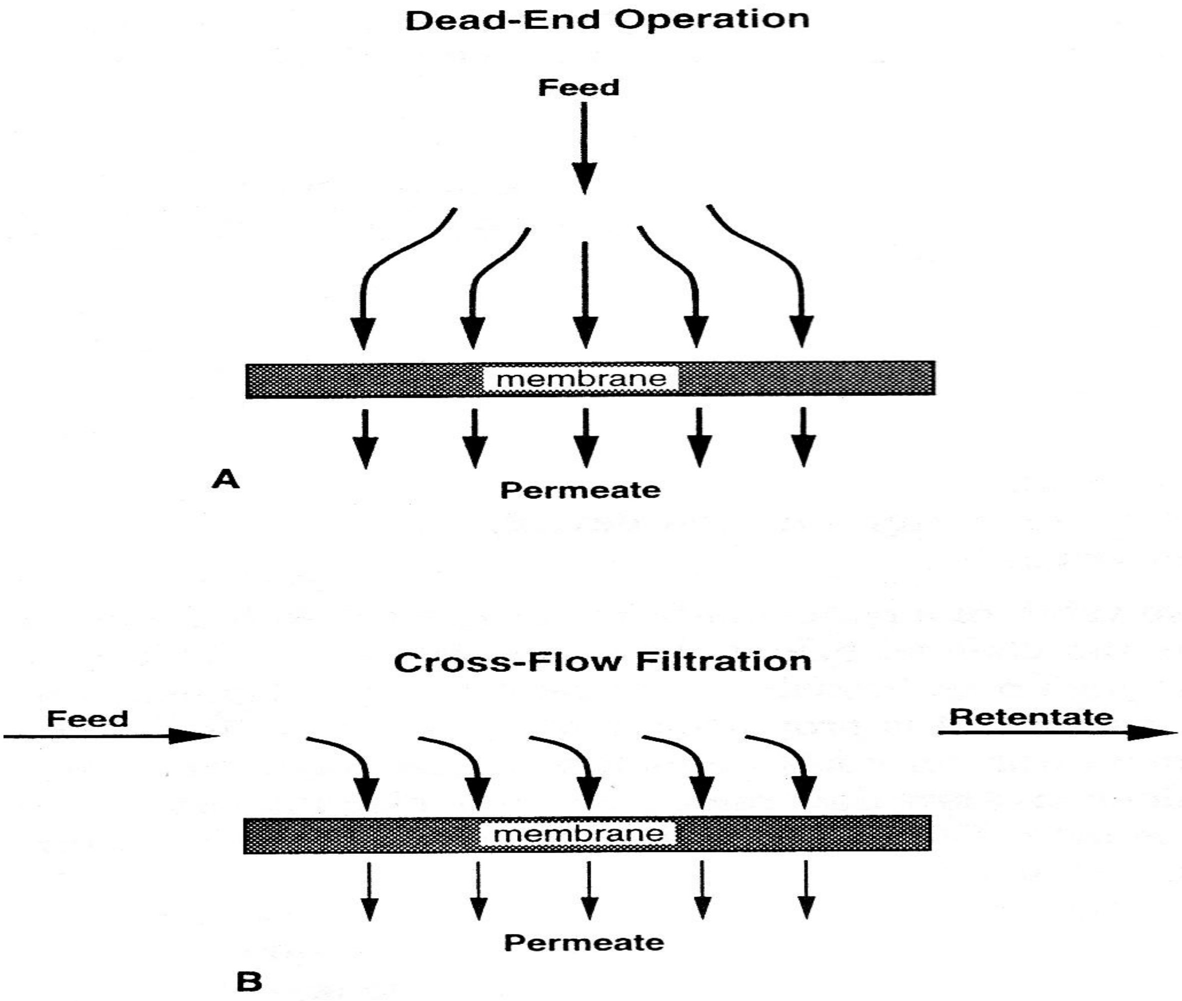


Fig. 1. 10 Dead end and cross flow filtration schematic. a) Dead end b) Cross flow [42].

The second operating mode is called the cross flow operating mode as shown in figure 1.10b. It involves moving the feed stream tangentially across the membrane surface while the permeate flows normal to the surface. In this operation mode there is one stream entering the membrane (feed stream) and two streams leaving the membrane (the permeate stream and the retentate stream). Cross flow filtration is effective against filter cake build up as the suspended solids that would have otherwise accumulated at the membrane surface are removed by the shear caused by cross flow at the membrane surface. Cross flow filtration finds wide use in streams with high solids, though it operation requires more energy. It is effective in filtration of a lot of streams. This thesis is confined to investigations concerning cross flow filtration.

1.9.5 Summary

Membranes find wide application in various industries from the pharmaceutical industry to space research. They are ubiquitous in various filtration and separation processes and have over the years been applied to more applications as membrane material technology improves. This study investigated membrane technology for the separation of E&P wastes due to the versatility of membranes in separating comparable streams in other industries. Streams with more recalcitrant constituents and higher suspended and dissolved solids have been filtered successfully on industrial scales using membranes [51]. This investigation to our knowledge presents the first opportunity where field water based E&P wastes are investigated using different membranes to create effluent that can be re-useable for oil-field purposes. It seeks to filter spent drilling waste to extract re-useable effluent and concentrate the waste volume and to filter produced water as a mechanical pre-treatment upstream of desalination.

Membranes represent the most suitable technology to test the hypothesis that filtration of water based E&P wastes at the colloidal and particle size range produce effluents suitable for re-use. Traditional filtration and or separation system such as hydrocyclones and centrifuges are limited on their filtration size lower limit and filtration using these technologies is usually aims at preparing the wastes for disposal not re-use. Also these traditional separation systems are energy intensive in their operation and have a large footprint when deployed to oil and gas sites. In comparison to these traditional technologies, membranes have low energy consumption and they also have very low foot print in comparison, these factors – the filtration size range, low foot print and energy consumption made membrane investigation the most rational technology for colloidal and particle size filtration of water based E&P wastes.

Waste volume reduction through solids concentration was another integral objective of this investigation especially for spent drilling fluid. Traditional separation technologies available in the oil field have low volume concentration especially in the 50 micron range and below while membranes are effective at concentrating waste volumes when the right pore size is chosen. This ability to effectively separate the waste and at the same time concentrate the waste volume made the investigation of membranes for solids laden-waste such as spent drilling fluids interesting and practical. The benefits of re-use, reduced foot print (through pit size reduction) and reduced waste volume disposal costs are concrete drivers that make this investigation not only of academic value but of practical value to oil and gas industry.

Volume concentration and filtration of colloidal and sand particles is not only essential for re-use wastes in oil-field applications but it also affords the use of environmentally friendly technologies such as bioremediation that are impractical due to the volume of wastes generated. If filtration of water based E&P wastes using membranes is achievable, other water based wastes such as fracture fluid backflow which are generated and disposed without re-use would also be open to similar investigations. This investigation intends to open the discussion at a more practical environmentally friendly look at water based waste management.

CHAPTER II

MATERIALS AND MEMBRANE CHARACTERIZATION

2.1 Introduction

The aim of chapter II is to describe the nature of the water based E&P wastes used in the experiments, how they were defined and how some degree of uniformity was achieved. A description of the experiment design and experimental procedures is also provided including schematics to give better comprehension. Membrane equipment operation procedure and maintenance is also explained along with the cleaning and treatment methods employed on the different membranes. Finally, equations used in calculating the parameters of interest from flux to fouling metrics are also listed in this chapter.

2.2 Sources and Uniformity of Drilling Wastes

The water based E&P wastes (produced water and spent drilling fluids) used in all experiments were procured from the field and were representative of wastes as produced during real operations. Produced water samples were supplied by Advanced Hydrocarbons, Graham Road, College Station, Texas. Advanced Hydrocarbons is a salt water disposal company that hauls salt water, fracture (frac) fluids and specialty chemicals from various oil and gas operations injecting them into underground storage wells (class II D injection wells). Advanced Hydrocarbon receives produced water from drilling and fracturing operations mostly in Texas and adjoining states in the south.

Produced water samples for the experiments were collected freshly when needed from the Advanced Hydrocarbon operation in College station. The samples were pumped directly from the hauling trucks to the 250 gallon collecting tanks for transport to the laboratory. The hauling trucks carried fresh produced water usually from a hundred miles location or more to the disposal site. About a hundred and fifty (150) gallons were collected each time for our experiments and samples were collected twice a week, samples after 72 hours were usually not used for experiments. Produced water when left to sit for a while changes and is markedly different from the original sample from the source, using the samples as soon as possible was an important objective. At the truck collection point the produced water is randomly sampled for temperature, pH, salinity, chloride and calcium to confirm if the sample was within our defined arbitrary range.

The spent drilling fluid was supplied by Newpark Drilling Fluids LLC, Texas, from the Chevron Carthage drilling operation. The drilling fluid used in all the experiments was a lignosulphonate water based drilling mud. This mud was transported from the field to the Texas A&M laboratory from the Carthage field operations in East Texas near the Louisiana state line. The spent drilling mud was from the mud pit and transported in sealed 55 barrel drums. A mud report (see appendix) came with each sample and after each sample was delivered it was sampled for the mud weight, viscosity, gel strength, pH, and salinity. All samples if not used immediately were kept in refrigerated storage rooms at the Texas A&M food protein laboratory till they were used. Samples were mixed vigorously before experiments especially after storage, dilution was necessary for samples allowed to seat for long periods although this was rare, efforts were made to use the samples as soon as they were delivered.

Uniformity of E&P wastes is a difficult concept to achieve in practice. Produced water from different formations or reservoirs differ in their composition chemically and physically and this also applies to drilling fluids. Spatial and temporal factors account for significant changes in the nature of these wastes. To make uniform the wastes used in the experiments, ranges were specified for the properties of interests and as much as possible samples from the same location with the same properties were sought. Sourcing similar waste from the same location worked in procuring spent drilling fluid as the mud company (Newpark Drilling Fluids) supplied the same operator (Chevron) the same mud type to drill the same type of formation in the same region (Carthage, Texas). For the produced water a range was specified for the parameters of interests namely- salinity, pH, solids concentration and the concentration of some divalent ions. Using portable measuring kits we were able to achieve some degree of uniformity based on our criterion.

Two types of drilling fluids represent about 90% of the water base drilling fluid used in drilling operations [53]. The first drilling fluid is the lignosulfonate drilling mud (recipe shown in appendix), this water base drilling mud is treated with lignosulfonate a chemical additive which is a byproduct of papermaking. Lignosulfonate is added as a constituent of the mud to cause deflocculation of solids and clay particles, this drilling fluid is used mostly in drilling wells with high bottom hole temperatures and in wells contaminated by calcium or salts. The second drilling fluid is the KCL polymer mud (recipe in appendix), the basis of the mud is the normally anionic encapsulating polymer fluid, potassium chloride, which is added to provide potassium ion that assists in stabilizing reactive clays particularly mixed layer clays in the formation [52,53]. Lignosulfonate based drilling muds are by far the most popular and was the mud of choice in this study. It differs from the KCL polymer muds rather slightly and the deflocculation of the solids poses a greater hindrance to filtration so it was chosen because it is the least filterable of both mud types.

2.3 Experiment Design

In the experiment design the first experiment carried out was membrane characterization of all membranes using reverse osmosis water (RO) water. This provided the baseline characteristic of the individual membranes. It shows how the operational parameters of transmembrane pressure (TMP), cross flow velocity (CFV) and temperature interacts with the membrane material and the pore size. This characterization shows us the optimum membrane operation using an ideal feed. Two membrane material types and module type were used in this baseline characterization; PVDF hollow fibre membrane and the ceramic tubular membrane. The hollow fibre membrane pore sizes were 0.1 and 0.2 micron while the ceramic membrane sizes were 0.005, 0.01 and 0.2 microns.

The next step was the determination of the effect of feed characteristics variation on the filtration of water based wastes (produced water and spent drilling fluids) using both membrane types (ceramic and hollow fibre). An arbitrary operational parameter set was determined and feed characteristic varied (an arbitrary feed characteristic set was also defined) during individual runs. The feed characteristics studied and varied were solids concentration for spent drilling fluids and oil concentration for produced water. Using the defined arbitrary operational parameter (pressure, transmembrane pressure and cross flow velocity) a variation of the feed characteristics was made using values above and below the defined feed characteristic to determine the effect variation had on filtration. The objective was to determine a suitable feed characteristic range for filtration of drilling wastes and also to define a feed for studying the effect of operational parameter variation. This was done using both membrane types.

After the feed characteristic variation of both waste types, the effect of the operational parameters- temperature, cross flow velocity and transmembrane pressure on the filtration of produced water and spent drilling fluid using both types of membrane types was determined. Variations against an arbitrary set of values for temperature, cross flow velocity and transmembrane pressure was carried out by varying a single operational parameter while holding the other operational parameter values constant. This variation of the single parameter was done above and below the arbitrary set value. Uniformity in the waste composition used in the operational parameter evaluation was preserved as humanly possible to ensure balanced comparison. After this set of experiments a suitable operational parameter set that best optimized filtration and reduced fouling was then determined and used for the next set of experiments.

Experiments were carried out to determine to determine the resistance calculation using only the ceramic membrane type, the data generated from flux decline curves was also used to determine if filtration could be explained using the constant pressure blocking laws filtration models [65,68]. Fouling mitigation techniques using clean permeate and or water was also carried out to determine the best method to prolong the onset of flux decline during filtration of these wastes using both types of membranes. Permeate and or clean water was used in backwashing to determine the efficacy of recovering the flux after flux decline during membrane operation. Most of the experiments were carried out three times and the graphs produced are an average of the three data points from each experiment. Experiment duration was usually 65 -80 minutes except during fouling and backwash experiments were experiments had longer durations between four to six hours.

Membrane cleaning studies were also carried out using two different cleaning solutions, the Divos 110 alkaline cleaning chemical and a patented aqueous surfactant solution supplied by a wellbore cleaning company. The cleaning solution effectiveness was compared against each other by determining their clean water flux recovery after filtration at conditions that consolidated fouling most especially after filtration at high transmembrane pressures. The procedure and experiment design used in the resistance calculation and chemical cleaning studies as well as the fouling mitigation studies are provided in the respective chapters where the results are presented.

2.4 Equipment

2.4.1 Filtration Unit

The filtration equipment used was a custom made filtration unit from the separations sciences department in Texas A&M. It has a 15 gallon feed reservoir from which a 5 HP rated centrifugal pump pumped the sample through the membrane filters. Upstream and downstream of the membrane housing are pressure gauges that measure the inlet and outlet pressure respectively. Flow passes through a flow meter at the feed outlet showing the flow through the membrane, a valve is used to control the flow rate from the pump. The flow from the membrane housing passes through a heat exchanger, using steam from the boiler or cool water from the cold water line, the temperature of the sample is kept regulated and there is a thermometer that reads the temperature of the sample.

For backwashing operations the alterations were made to the module where a tube from an exterior pump was used to flow permeate/pure water in reverse flow to the filtration flow at high cross flow velocity, another tube at the other module end leads the flush out. During backwash the permeate valve is shut off. The filtration equipment had the capacity to take three membrane housing in parallel, but only one membrane housing connection was used for all experiments. For the hollow fibre membranes connections were made that allowed the operation of the hollow fibre membranes to be used in the same filtration system as the ceramic membranes. These connections also allowed for backwash of the hollow fibre membranes. Integrity tests were carried at all connections to make sure there were no air leaks during backwash, also pressure readings confirmed if there was a leak present. To run the tests with a different micron size, a different ceramic or hollow fibre module with the pore size rating needed is fixed into the membrane housing. Figure 2.1 shows the schematic of the filtration equipment and figure 2.2 shows filtration when backwashing was used for fouling mitigation.

In the fouling mitigation investigation, backwashing was investigated. For the clean permeate backwash the filtration equipment had to be modified using valves and pipes to channel clean permeate to the membrane in the reverse direction, to do this an additional pump was used (not shown), figure 2.2 shows a schematic of the modified filtration unit to allow for the clean permeate backwash. Some tests were carried out with a 10 micron membrane filter upstream of the membrane housing inlet after the pump to prevent clogging when using the PVDF hollow fibre membrane. This was in cases where feed contained a lot of irregularly shaped solids.

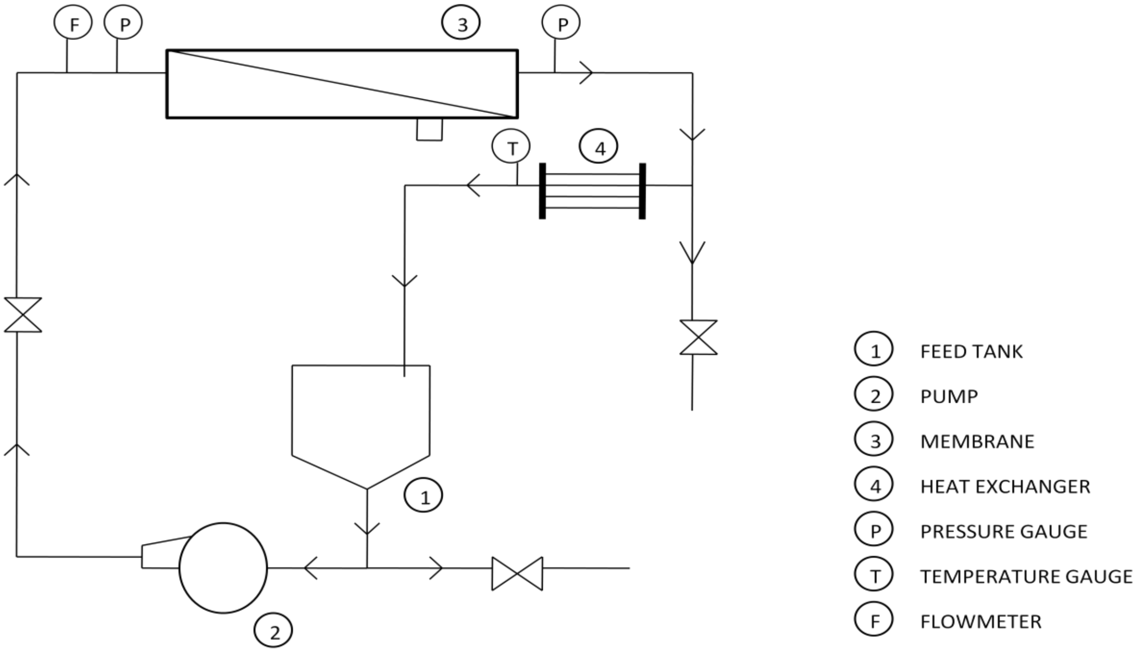


Fig. 2. 1 Schematic of filtration process.

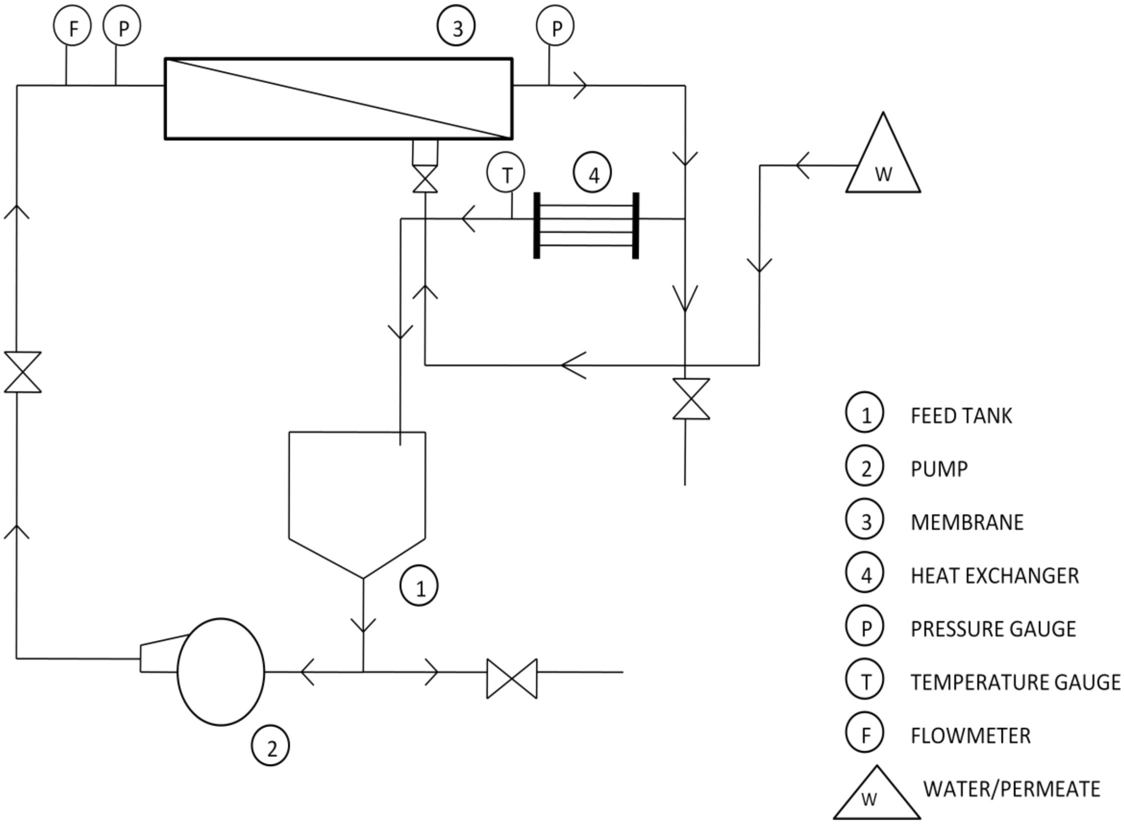


Fig. 2. 2 Filtration process modified for fouling mitigation.

2.4.2 Laser Particle Counter

The Spectrex PC- 2200 laser particle analyzer laser particle counter manufactured by Spectrex, California was used for solids particle analysis. Utilizing the principle of "near angle light scatter", a revolving laser beam passes through the walls of a glass container where it is directed through a central "sensitive zone where the equipment not only counts the particles in suspension but tabulates their size as well. The analog signals generated by the light pulses are routed to a computer and digitized. Feed samples of both drilling fluids and produced water were analyzed before each run, permeate samples were also analyzed before each run and retentate samples were also analyzed before each run.

2.4.3 Salinity and pH Reading

The HACH Sension 156 portable multi parameter measurement device was used to read the salinity of the samples by inserting the electrodes into about 100 mL of the sample and the salinity of the sample was read digitally. Feed samples, permeate samples and retentate samples salinity was recorded for the all samples processed. For the drilling mud the salinity was read the same way and the salinity value was checked with that in the mud report that came with the mud samples.

The pH of the sample was also read using the HACH Sension 156 portable multi parameter measurement device. It was used to read the pH of the samples by inserting the electrodes into about 100 mL of the sample and the pH of the sample was read digitally. Feed samples, permeate samples and retentate sample pH was recorded for the all samples processed.

2.4.4 Turbidity Reading

The HACH turbidity meter was to measure the turbidity of all samples. The samples are put into a 10 mL bottle in the bottle receptacle and covered, then light rays are then passed through the bottle and the deflection of the light rays are then quantified to give a reading. Feed samples, permeate samples and retentate sample turbidity was recorded for each experiment run.

2.4.5 Chemical Analysis Reading of Produced Water

Though ultrafiltration and microfiltration do not affect the separation of dissolved solids, for sample collection at the produced water disposal facility the dissolved solids needed to be measured to determine if the sample was within the arbritrary range set. Ion selective electrodes (ISE) from Laval lab in Canada were procured and electrodes for measuring calcium and chloride were used to determine the concentration of the ions in the samples. The permeate concentration of these ions did not usually change after filtration.

2.4.6 Temperature Reading

The temperature of the sample was read using the HACH Sension 156 portable multi parameter measurement, this was done by inserting the metal electrode into the samples directly and the temperature of the sample was read digitally. Feed samples, permeate samples and retentate samples were read for the all samples processed. It was also used to cross check the accuracy of the temperature gauge on the filtration equipment.

2.4.7 Oil in Water Concentration

The TD 500 oil in water analyzer manufactured by Turner systems was used to measure the oil in water concentration. The TD 500 analyzer measures the oil content in oily waters containing crude oil or gas condensate and it finds wide use in the oil and gas industry. It measures the oil content by UV fluorescence using an easy solvent extraction with high accuracy and reproducibility. The standard procedure of solvent extraction is specified by EPA - 1664A method and the analysis is compatible with common solvents such as hexane, Freon, Xylene amongst others. The TD 500 was calibrated using a San Francisco crude oil with 39 API and a calibration curve was made based on the known concentration response to UV.

2.5 Experimental Procedure

Before each run the clean water flux of the membrane is recorded at a set temperature, transmembrane pressure and cross flow velocity with reverse osmosis water. The feed tank is then filled with the samples and pumped through the membrane, the operational parameters are set blow the required values and filtration is allowed for about ninety (90) seconds. After ninety seconds, the operational parameters are then set to the desired flow rates and filtration of the sample continues. Using steam or cold water, temperature regulation is achieved using the heat exchanger. The pressure of the feed inlet and outlet are recorded manually on the data chart as well as the permeate volume, sample flow rate and temperature of the samples. The permeate volume is manually measured using a stopwatch and a measuring cylinder, the permeate volume is measured three times and the average of the three readings is recorded as the point value.

After each experiment the clean water flux is recorded, then the membrane is flushed at higher cross velocity and low pressure using reverse osmosis water, using the initial temperature, transmembrane pressure and crossflow velocity the original clean water flux was taken to see how much of the flux is recovered. In the event that considerable flux is lost, chemical membrane cleaning is usually carried out to restore the flux to its original comparable level, clean water flux less than 90% required chemical cleaning. To address fouling propensity due to amount of runs especially during normal filtration and repeats most filtration experiments were run for not more than seventy (70) minutes and were run for longer duration for the fouling and backwashing experiments. Using the membrane size measurements and manually recorded measurements, the flux, yield, concentration values and fouling parameters were calculated.

2.6 Analytical Formulae

Membrane filtration has different purposes in separation of liquid streams; it might be to concentrate the solute or to reduce the volume waste or to extract a component of the solution. Whatever the purpose of filtration certain metrics are required in measuring if filtration is feasible and to determine methods of improving filtration. With respect to the intent of separation of water based wastes namely the removal of suspended solids and volume reduction, metrics such as permeate flux, rejection, recovery and volume rejection are essential in determining the feasibility of water based wastes membrane filtration.

1. Flux (J)

Filtration feasibility is determined by the amount of membrane area used and the permeate flux produced. The ideal is to use minimal membrane area to produce larger permeate flux, this saves on energy, space and brings good economic return on filtration. The membrane flux is expressed in terms of the unit membrane area with respect to the permeate volume collected in unit time. Flux is defined as

$$Flux = \frac{Permeate\ volume\ collected}{membrane\ area\ \times time} \tag{2.1}$$

Flux can be calculated in liters per m^2 per hour (LMH) or it can be calculated as it is in this thesis in gallons per ft^2 per day (GFD), the day is not corrected for 8 hour operation and remains a 24 hour day. Pure water flux (J_w) differs from the permeate flux as it measures the permeate flux using RO water as the feed under specified conditions of temperature, pressure and cross flow velocity, it is an essential measurement in membrane fouling studies.

2. Rejection (R)

Rejection relates to the amount of the solute quantity that is left behind in the membrane. Rejection shows the efficiency at which the membrane separates the species of the feed that needs to be separated either to claim permeate or the retentate. In this thesis the species to be rejected would be the solids concentration (spent drilling fluids) oil-concentration (produced water), it is measured as

$$R = 1 - \frac{Cp}{Cf} \tag{2.2}$$

where R is rejection, C_p is the concentration of the species in the permeate and C_f is the concentration of the species in the feed. Rejection can also be reported in percentage by multiplying by 100.

3. Recovery (Y)

Recovery is defined at the amount of the feed that is treated; it is an estimation of the performance of a membrane system. It measures the volumetric fraction of the permeate to the feed showing how much of the permeate is recovered from the feed.

$$Y(\%) = \frac{Qp}{Qf} \times 100 \tag{2.3}$$

Where Y is the recovery, Qp the permeate volume and Qf the initial volume of the feed.

4. Concentration Factor (CF) and Volume Reduction (VR)

The concentration factor or the concentration ratio is the ratio of the initial feed volume (or weight or flow rate) to the retentate volume (or weight or flow rate). When volume is considered it is called the volume concentration ratio (VCR)

$$VCR = \frac{Initial\ feed\ volume\ (Vo)}{Retentate\ volume (Vr)}$$

(2.4)

Volume reduction is the amount the feed volume has reduced; it is represented by comparing the volumes of the feed at the end of filtration to the volume initially

$$VR = \frac{V\ (final)}{V(initial)}$$

(2.5)

Using mass balance it is seen that concentration factor, the rejection and recovery are linked

$$CF = 1\ + R(\frac{Y}{1-Y})$$

(2.6)

Equations dealing with fouling and fouling mechanisms are presented in the chapters where the results are discussed.

2.7 Membrane Characterization

2.7.1 Introduction

This chapter is designed to generate a baseline description of the membranes used during the filtration experiments using reverse osmosis (RO) grade water. This description illustrates the basic characteristic of the individual membranes and how the operational parameters of transmembrane pressure (TMP), cross flow velocity (CFV) and temperature interacts with the membrane material and pore size to determine the filtration capacity of the membrane when a solids free feed is filtered. RO water is water devoid of any ions; the RO water used in this membrane characterization was made by running tap water through a reverse osmosis filter. This device also ensures the removal of microorganisms through treatment by UV radiation downstream of the filter.

The ceramic membranes were manufactured by Corning Membranes. The membranes were made from α-Alumina (0.2 micron), Silica (0.005 micron) and Titania (0.01). The general properties of membranes are described in chapter I. Three average pore size membranes were used in our investigation; they are the 0.005 micron, 0.01 micron and the 0.2 micron membranes. The dimensions of the ceramic membranes are 305 mm in length, 27 mm in diameter and an effective membrane area of 0.13 m^2. The ceramic membranes are monolith membranes and a pictorial depiction of a ceramic membrane is shown in figure 1.9.

The hollow fibre membranes were procured from Pall microfilters, they are the called the microza membranes and were developed in Japan, they are made from polyvinylidene fluoride (PVDF) and are hydrophobic membranes. Two average pore size membranes were used in our investigation they were 0.2 micron (UMP 153) and 0.1 micron membrane (USP 143). The membranes have a 1.4 mm internal diameter and a 2.2 mm outer diameter. The 0.2 micron filter have bounded hollow fibre bundles giving an effective membrane area of 0.8 m^2 and the 0.1 micron filter have bounded hollow fibre bundles giving an effective membrane area of 0.12 m^2. A pictorial depiction of a hollow fibre membrane is shown in figure 1.8.

Studies [54,55]show that membrane properties such as pore size, membrane material and operational parameters (temperature, TMP and CFV) determine the filtration ability of membranes making feed characteristic the other determinant in the applying membranes to a particular stream. In this ideal feed membrane characterization, the relationship between membrane property and operational parameters (temperature, TMP and CFV) are investigated to describe their relationship. This is designed to serve as a baseline description of the membranes and present a basis for operational parameters used in experiments with actual feed (water based E&P wastes).

In membrane filtration especially in microfiltration (MF) and ultra filtration (UF), permeate flux is seen to directly increase with increase in transmembrane pressure [56] for cases where there are conditions of low feed concentration and high feed velocity [40]. In the absence of these conditions (low feed concentration and high feed velocity) fluxes becomes independent of pressure and permeate flux is mass transfer controlled, incremental pressure would not bring about an increase in flux. The region where pressure increase directly influences flux by increasing flux is known as the pressure controlled region. Transmembrane pressure is also an important factor in fouling of membranes; pressure regimens control the activities of gel layers on the membrane surface and determine the rate of flux decline.

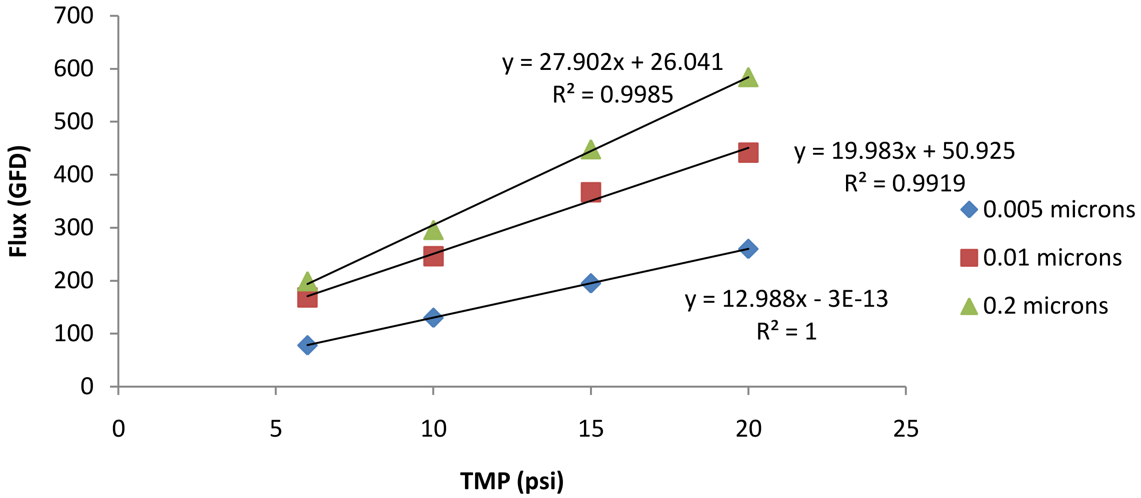


Fig. 2. 3 Effect of TMP on the RO permeate Flux for the ceramic membrane at CFV of 8.04 ft/s at 22 C.

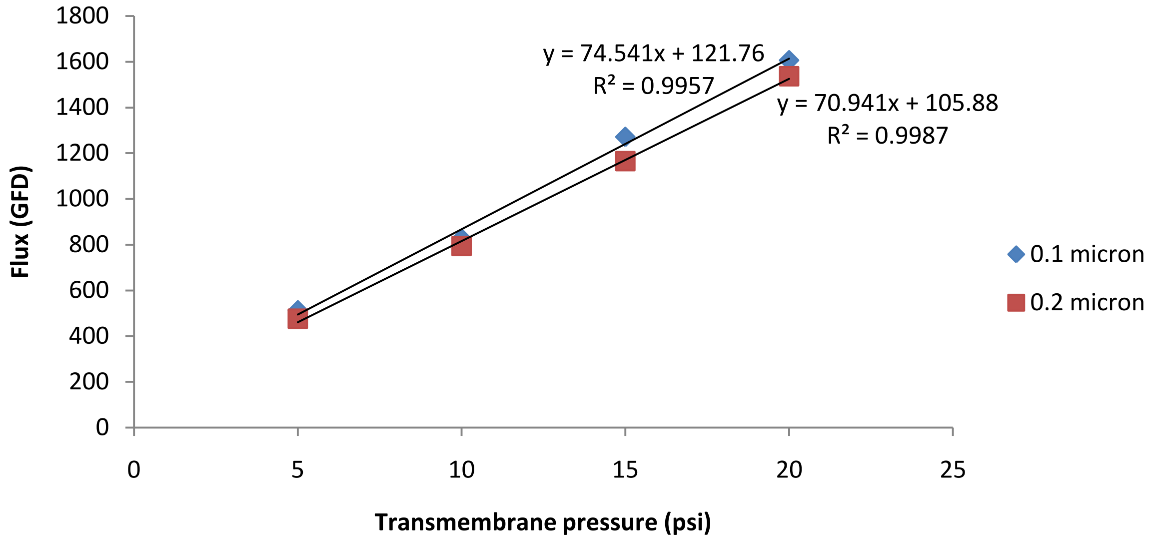


Fig. 2. 4 Effect of TMP on the RO permeate Flux for the hollow fibre membrane at CFV of 3.84 ft/s at 22 C.

As seen from figures 2.3 and 2.4 there is a close to perfect linear correlation between transmembrane pressure and flux in both the ceramic membrane and the hollow fibre membrane at the chosen cross flow velocity and temperature. Flux at additional cross flow velocities and temperatures were also carried out and the same linear correlation was observed. This linear correlation is expected as we have all the requisite conditions – low feed concentration and high feed velocity for filtration to be pressure controlled.

As expected flux is higher in membranes as the pore sizes increase at comparative pressure, cross flow velocity and temperature and this is due to the fact that membranes with larger pores sizes have lower membrane resistance (R_m) and as such would have higher permeate fluxes. At lower pressures (less than 10 psi) at the same cross flow velocity the flux between the 0.2 and 0.01 micron membranes seem to be closer but at higher pressures the increase in flux with pore sizes becomes apparent. This would seem to give an indication of the sensitivity of permeate flux to transmembrane pressure at larger pore sizes. It seems that the larger the pore size the greater the sensitivity transmembrane pressure has on the permeate flux, thus it can be inferred that in pressure controlled region of the flux profile larger pore sizes are more sensitive to increases in transmembrane pressure.

With the hollow fibre membrane results we see that permeate flux increases slightly with pore size at comparative pressure, cross flow velocity and temperature. The flux difference between both micron sizes of the hollow fibre membranes is smaller when compared to the flux difference between proportional pore sizes of the ceramic membranes. The reason for this disparity in the pore size flux difference could due to the fact that the effective membrane area of the 0.1 micron hollow fiber membrane is greater than that of the 0.2 micron hollow fibre membrane due to the higher number of hollow tubes packed in the 0.1 module. Comparing flux of both membrane types, we see that the hollow fibre membranes have higher fluxes at the about the same pressure and at lower cross flow velocity, this is due to the large surface area to volume ratio of this membrane [50].

Cross flow velocity is the rate at which the feed flows over the membrane area and the cross flow velocity (CFV) at which membranes are run is essential for various reasons as shall be discussed later. CFV has a large effect on the flux in the mass transfer controlled region i.e. the region where pressure increase does not affect the flux. Cross flow velocity is also essential as more feed is pumped through the membrane without fouling higher yields are attained. Also higher cross flow velocities dictate how much pumping energy is expended in operating membranes. Ceramic membranes traditionally have to be run at comparatively high CFV relative to hollow fibre membranes due to the recirculation frequency of the retentate because of its low surface area to volume ratio, therefore running ceramic membranes require more energy than the low cross flow rated hollow fibre membranes.

Most tubular membranes units operate under turbulent conditions with high Reynolds numbers usually greater than 10,000. This translates to a high feed flow through the membrane and a lot of turbulence generated during filtration. In contrast the hollow fibre membranes operate at laminar conditions with Reynolds number of usually less than 3000, though they operate at laminar flow shear rates are also high in hollow fibre due to a combination of thin channels and high velocity, Cheryan [40] reports that shear rates ay the walls could be between 12,000 – 16000 sec^{-1}.

Ceramic membranes are run at average of about 6 – 16 ft/s while hollow fibre membranes are run at about 2-5 ft/s [49]. CFV also helps in prolonging the onset of fouling as it can be used in controlling the gel-layer as shall be explained later. The ceramic membranes were run at four velocities, 6.04 ft/s, 8.04 ft/s, 11.09 ft/s and 14.11 ft/s all corresponding to flow rates of 6, 8, 11 and 14 gallons per minute. The hollow fibre membranes are rated for low operating velocities, for the 0.2 hollow fibre membranes two cross flow velocities of 3.48 ft/s and 6.59 ft/s were used corresponding to 4.5 and 8.5 gallons per minute respectively while for the 0.1 micron membrane two cross flow velocities of 3.81 ft/s and 6.69 ft/s were used corresponding to 4.0 and 7.0 gallons per minute respectively were used.

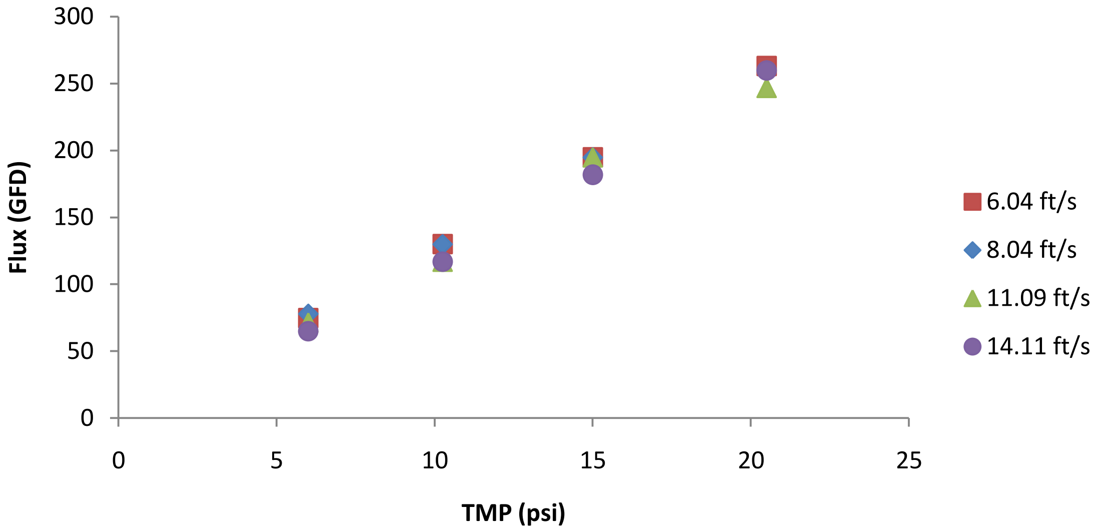


Fig. 2. 5 Effect of cross flow velocity on the 0.005 pore size ceramic membranes .

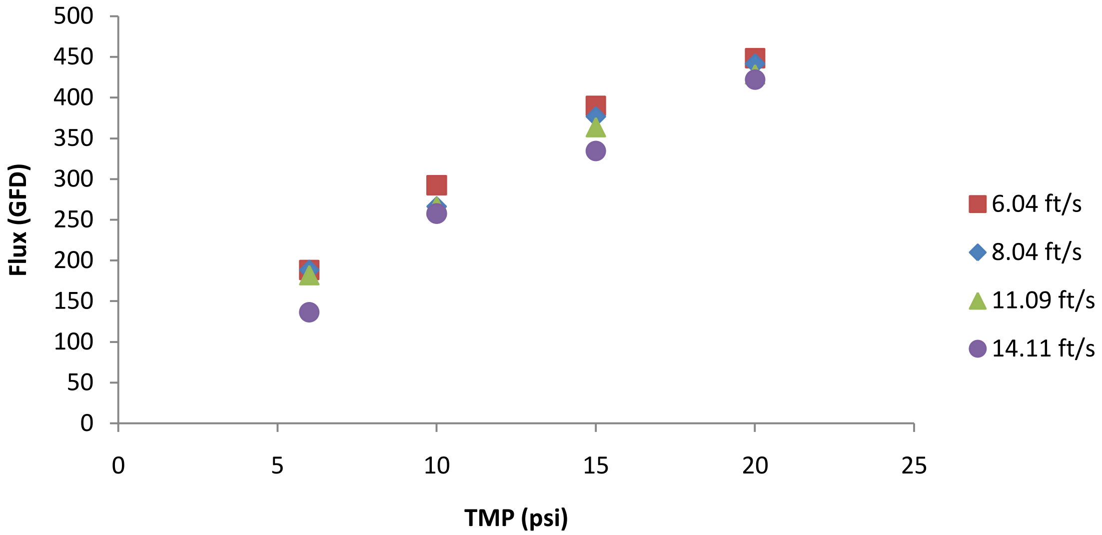


Fig. 2. 6 Effect of cross flow velocity on the 0.01 pore size ceramic membranes.

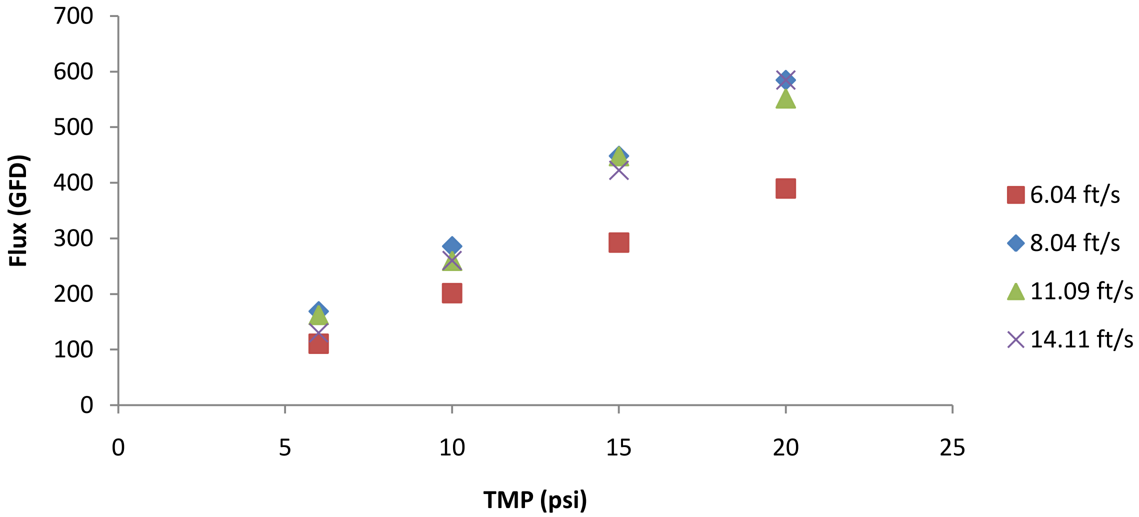


Fig. 2. 7 Effect of cross flow velocity on the 0.2 pore size ceramic membranes .

From figures 2.5-2.7 where the cross flow velocities are varied at different pressures, we can see that there is no significant effect of high cross flow velocities on the flux as the flux remains nearly the same with increases in cross flow velocities. This is because the system is still in the pressured control region and experiences no fouling thus the pressure continues to be dominant in determining flux increase. The nature of the feed (RO water) where there are no solutes being deposited on the membranes or even if there were any deposition of solutes, the cross flow velocity is high enough to prevent fouling of the membrane surface creating a condition where mass transfer has no effect. When filtering drilling wastes that have higher feed concentrations than the RO water, the effect of higher cross flow velocities shall be apparent.

The same observation as noted with ceramic membranes was also observed in the hollow fibre membranes as seen in figures 2.8 and 2.9.

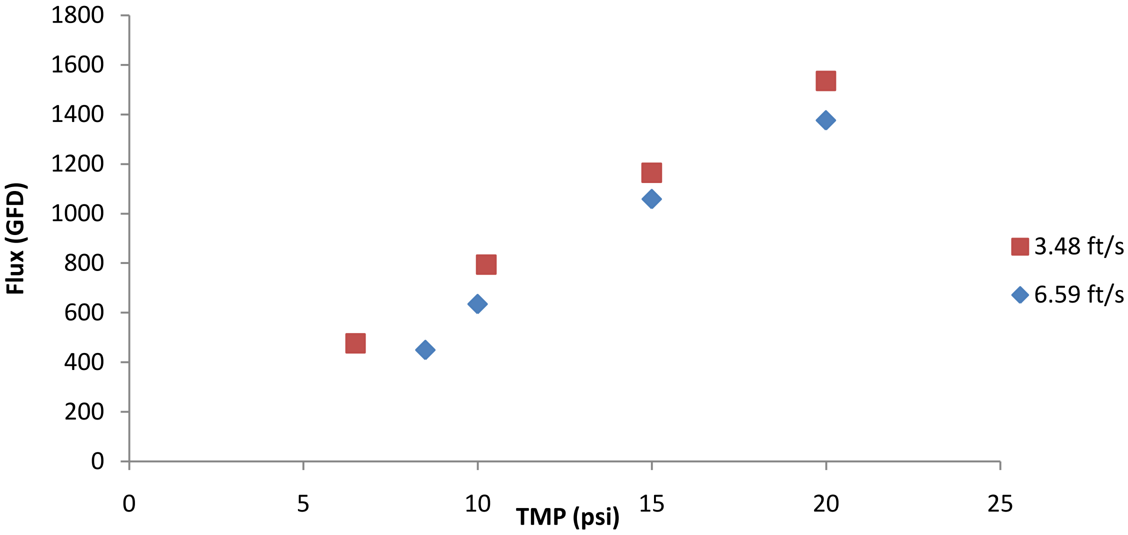


Fig. 2. 8 Effect of cross flow velocity on the 0.2 pore size hollow fibre membrane.

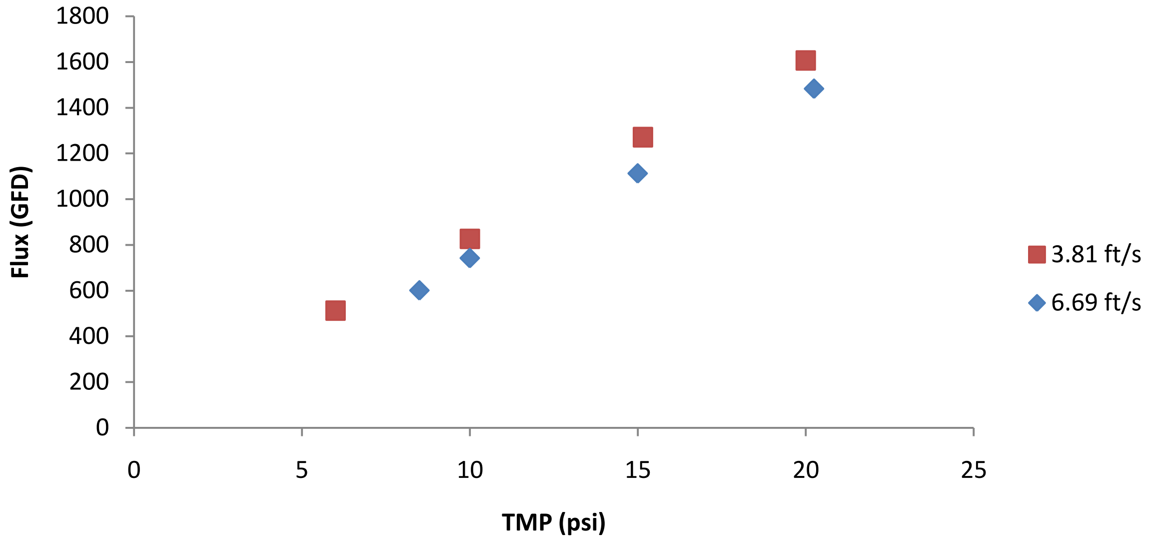


Fig. 2. 9 Effect of cross flow velocity on the 0.1 pore size hollow fibre membrane**.**

Comparing the flux at the different cross flow velocity for the different pore sizes we come up with the same conclusion as in figures 2.5 and 2.6 that flux increases linearly with the pressure and that the effect of cross flow velocity is minimal in the pressure controlled region.

In the absence of fouling and of the membranes or deposition of solutes on the membrane, increase in temperature results in higher fluxes; this increase in flux is attributed to the effect of temperature on fluid density and viscosity [56]. Temperature reduces the viscosity of the feed solution reducing the cohesive molecular forces while simultaneously allowing the greater increase of molecular interchange with the former more pronounced than the former causing a reduction in the viscosity of the feed [40]. Since the membrane characterization occurs in the pressure controlled region the effect of temperature on the flux is solely due to its effect on fluid density and viscosity.

Figure 2.10 illustrates the effect of temperature on the permeate flux in the membrane characterization using RO water. It was observed that flux increased linearly with temperature. For the 0.2 micron ceramic membrane flux increased from approximately 260 GFD to 345 GFD in a 23 ^{o}C rise in temperature, it is believed that in practical terms, it would take a temperature rise of 30-45 °C to double the flux [40,57] and our observation seems to validate the claim. The same correlation was observed in the different ceramic pore sizes (0.005 and 0.01).

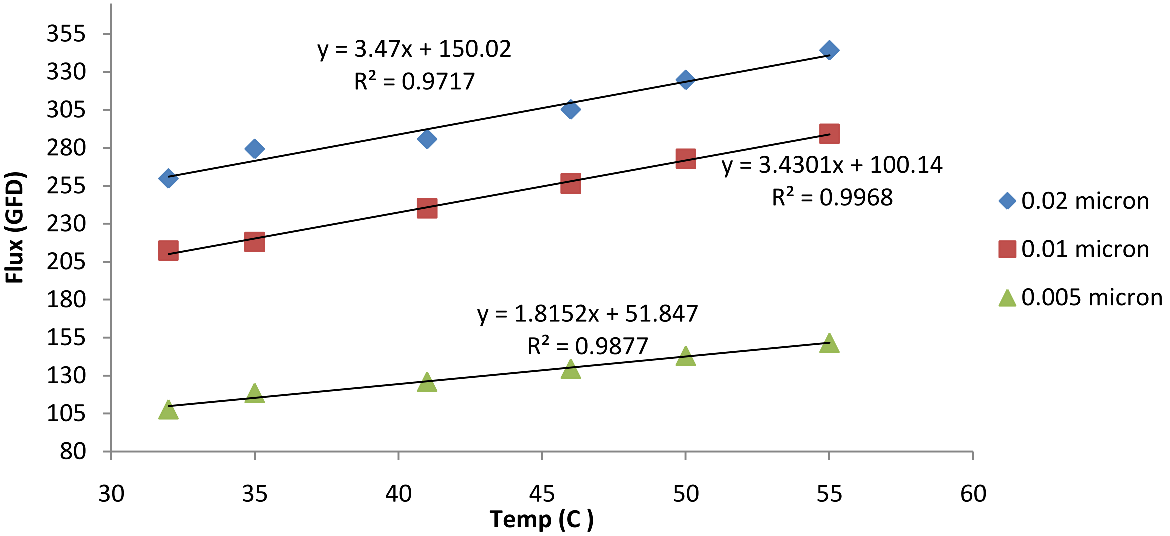


Fig. 2. 10 Effect of Temperature on flux of ceramic membranes (CFV 8.04 ft/s, TMP 15).

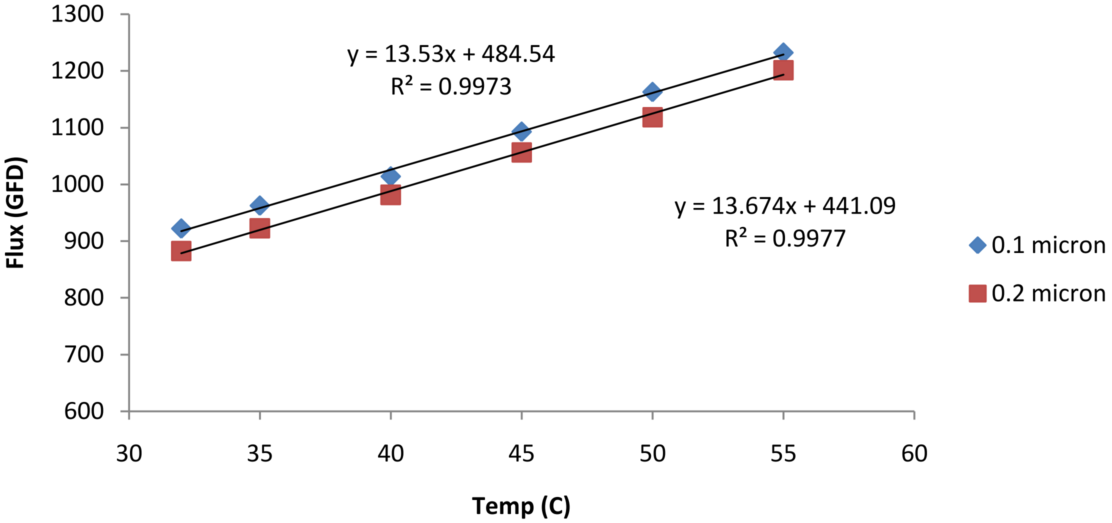


Figure 2. 11 Effect of Temperature on flux of hollow fibre membranes (CFV 3.81 ft/s, TMP 9.5).

The same linear correlation was observed in the relationship between temperature and flux using the hollow fibre membranes as illustrated in figure 2.11.

2.8 Summary

This chapter describes membrane characterizations using the three most important operational parameters in membrane filtration namely transmembrane pressure, cross flow velocity and temperature. The fluxes recorded here would be the maximum achievable fluxes due to the nature of the feed sample, it would be expected that the actual fluxes would be reduced in the filtration of water based E&P wastes particularly the filtration of spent drilling fluids. In the actual filtration of spent drilling fluids the effect of the solids concentration in the feed would affect filtration as mass transfer dynamics would be prominent. With respect to resistance, membrane resistance shall interfere in the filtration process, resistances due to concentration polarization, adsorption, reversible and irreversible fouling shall all affect the operation parameters and ultimately the flux.

It is observed that the larger the pore size the larger the permeate flux. For the colloidal filtration of water based E&P wastes the pore size choice of the membranes needs to be balanced against the needed permeate solids distribution, the propensity of fouling and maintaining the desired flux to make filtration feasible. The permeate solids distribution should be in the range needed for re-use, for example in the pre-treatment of produced water for desalination using reverse osmosis membranes, if the feed can be treated to 5 NTU or less, desalination is optimized thus membranes can serve as a mechanical pre-treatment for desalination. The propensity for fouling should be low when choosing a pore size, if pore sizes are to small permeate flux might not be practical and if pore sizes are too large fouling propensity increases.

The permeate flux also increased linearly with transmembrane pressure and temperature. The nature of the feed masked the complex relationship between pressure and flux in the mass controlled region as it is rarely linear. Pressure rise without subsequent rise in permeate flux is indicative of fouling thus pressure differences are important in membrane filtration fouling analysis. Also the pressures at which membranes are run (depending on their pore size) are important in aiding or delaying fouling. High pressures during filtration using large pore membranes with feed with particles size aggregates a lot smaller than the membrane pores accelerate pore plugging when compared to low pressures [40,49,56]. Temperature effects are dependent on the feed solution especially its viscosity and fluid density, less viscous feed would aid better filtration than a more viscous feed.

The other purpose of the membrane characterization was also to find a way to rationally arrive at a reasonable standard operating parameters for filtration experiments using water based E&P wastes see Tables 2.1 and 2.2. Experiments shall be carried out where the operational parameters of pressure, cross flow velocity and temperature shall be varied, to determine the effect each parameter on the membrane filtration of the two drilling wastes of interest i.e. produced water and spent drilling fluids. These variations shall be compared to the standard operating parameters from the membrane characterization to determine their effect. From the characterization we arbitrarily with enough reason define the standard operating parameters for the different membrane types as follows.

Table 2.1 Standard operating values for the hollow fibre membrane

Parameter	Arbitrary Standard Value
Transmembrane Pressure (psi)	10
Cross flow Velocity (ft/s)	3.48
Temperature (^{o}C)	38

Table 2.2 Standard operating values for the ceramic membrane

Parameter	Arbitrary Standard Value
Transmembrane Pressure (psi)	15
Cross flow Velocity (ft/s)	8.04
Temperature (^{o}C)	38

CHAPTER III

FEED AND PARAMETER VARIATION

3.1 Introduction

In this chapter the results of the filtration of water based wastes i.e. spent drilling fluid and produced water using ceramic tubular and hollow fibre membranes is reported. Filtration experimnets involved varying the feed parameters and the operational parameters of both water based wastes types below and above the arbitrary parameter value to determine their effect using the two membranes types. Observations were made and the description of the results are reported as well as compared against existing literature. Intra and inter membrane filtration results comparison is also made in reporting the results.

3.2 Drilling Mud Filtration

3.2.1 Parameter Variation of Drilling Mud Filtration

Feed samples for filtration of spent water based drilling mud were transported directly from the field and sent to the laboratory, each sample came with a mud report and a mud check was carried out in the mud lab to confirm details of the report. The feed parameter of interest in the filtration of spent drilling waste was primarily solids concentration and volume concentration was the intent of filtering spent drilling waste. The arbitrary spent drilling waste was defined to have 8.8± 0.5% solids per volume (19,000± 7000 mg/L) and a pH of 9.5± 0.3. Initial feed volume was 8 gallons for normal filtration experiments, the experiments were run in a batch mode and at full recycle mode i.e. permeate was channeled back to the feed tank. Arbitrary operating parameters for ceramic filtration was defined as a cross flow velocity of 10.08 ft/s, transmembrane pressure of 15 psi and temperature of 38 C. Temperature was varied between 20 and 52 C, transmembrane pressure varied between 10 and 20 psi and cross flow velocity varied between 6.04 and 16.12 ft/s. The feed parameter of interests was also varied, solids were varied between 8.8± 0.5% and 10.20± 0.15 % per volume (19,000± 7000 mg/L to 32,000± 4000 mg/L) .

Spent drilling mud filtration was carried out using ceramic membranes alone. This was decided because of the particle size concentration of the spent drilling mud, at these solids concentration hollow fibre membranes would be fouled with no appreciable flux. No screening was done upstream of the ceramic filter, the sample was pumped directly through the membranes. The schematic of the filtration process is provided in chapter II, in practical terms this would mean wastes from the mud pits being filtered directly. The results of the filtration process are reported below.

Results

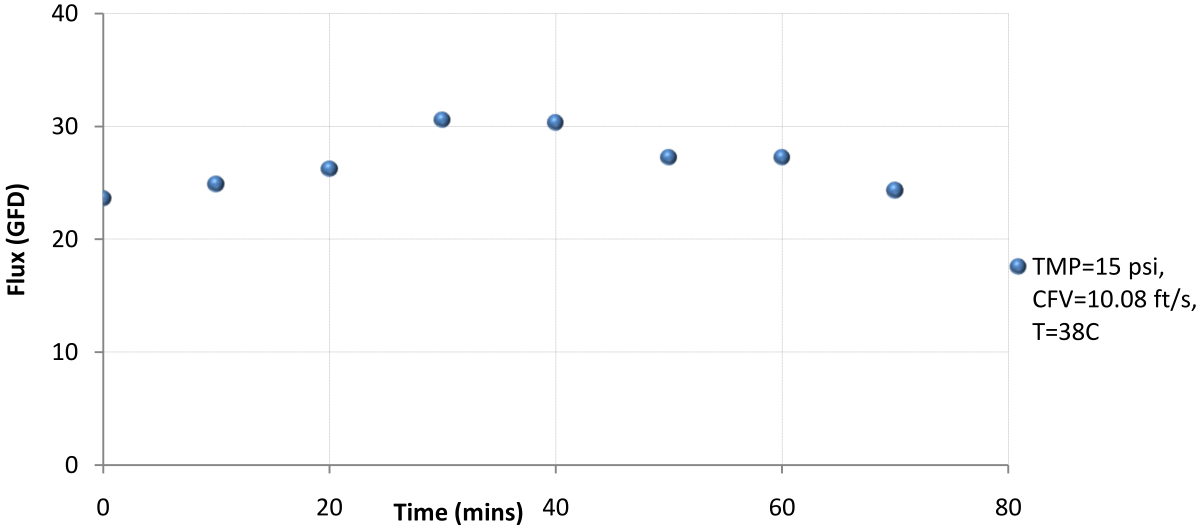


Fig. 3. 1 Ceramic filtration of spent drilling. Solids concentration (8.8± 0.5% vol) and pH (9.5). Ceramic membrane pore size (0.005 micron), transmembrane pressure (15 psi), cross flow velocity (10.08 ft/s) and temperature (38 C).

In the ceramic filtration of spent drilling fluid with solids concentration of 8.8± 0.5% solids per volume and a pH of 9.5, filtering at a transmembrane pressure of 15 psi, cross flow velocity of 10.08 ft/s (corresponding to 10 gallons per minute (gpm)) and temperature of 38 C, the average flux was 26.8 gallons per foot square per day (GFD), maximum permeate flux was 30.57 GFD and the lowest flux was 26.31 GFD, see figure 3.1. Flux decline for the experiment period was less than 20% of the highest recorded flux and there was no significant pressure increase during the experiment. There was 95 % rejection of the solids by the membrane as the feed solids concentration and permeate solids concentration was 18061 mg/L and 774 mg/L respectively. The volume concentration factor was 1.33 and the volume reduction was 0.75 i.e. the final volume was 75 % of the initial volume. Filtration for this duration and at these condition extracted 25% of the feed for reuse i.e. clean useable effluent for oil-field uses was 25% of the initial waste volume.

In the filtration of spent drilling fluids, like in the filtration of feeds with hydrocolloids and solids, solvent passes through the membranes and particles below the pore size remain on the membrane side where they tend to form a layer on the surface of the membrane. The initial rise in flux (between 0-30 minutes) occurs at the period where the wall is still being formed on the surface of the membrane and resistance to permeate passage is minimal. As filtration proceeds the wall is believed to be taking shape and resistance to the flow of permeate starts to increase with the build-up and it results in the onset of flux decline as less permeate percolates through the membrane. At this stage in filtration (the onset of flux decline) the effect of cross flow is lower than the energy needed to disrupt the formation of the wall; thereby it is believed that the wall layer is getting stabilized. The nature of the wall formed could range from viscous to gelatinous depending on the nature of the constituents of the feed [49].

The alternative explanation is that particles in the feed smaller than the pore sizes of the membrane plug the pores of the membrane. As the pores becomes constricted the flow of permeate is obstructed thereby creating hydraulic resistance to filtration. Progression of pore blockage would create a wall on the membrane surface when there is a saturation of particles in the pore spaces. The particle size distribution of the feed shows no particles smaller than the pore size (0.005 micron) due to equipment threshold thus pore plugging cannot be totally ruled out though the nature of the solids in drilling fluids might make this plausible. Most models used in trying to simulate high solids feed filtration use spherical glass beads that retain their shapes and sizes through most of filtration. In reality drilling fluids have varied particle sizes and at high shear would break to form smaller particles especially at high cross flow velocities if they break to sizes below the pore size then pore plugging could be possible.

If the flux decline is due to the cake layer formed at the membrane surface, the layer is known by different names to different authors. It is known as the “gel layer”, “CP layer”, “filter cake”, “particle wall” or “polarization layer” [40,49,64,69]. Concentration polarization (CP) layer shall be adopted in this thesis. The CP layer is assumed not to be chemical in nature but rather of a physical nature with varying degrees of attachment of the particles to the membrane surface. The CP layer can be altered through varying operational characteristics during filtration particularly cross flow velocity; water flushing at higher cross flow velocities reclaims the membrane flux in most degrees of concentration polarization. The inert nature of ceramic membrane materials reduces the reactivity of the membrane to feed dissolved constituents thereby lowering the propensity of chemical fouling but fouling by minerals and organics in the feed can contribute to flux decline apart from particle and colloidal deposition.

Concentration polarization can have enormous influence on flux decline. Bruin et al [58] reported a drop to 5% of the initial flux in the ultrafiltration of skim milk using a dead-end cell without agitation in 25 seconds. One of the major advantages of cross flow filtration over dead end filtration is the ability to control the effect of concentration polarization or the formation of the layer. There are two solids phases in water based drilling muds and both phases are suspended in the liquid phase of the mud.

One solid phase called the reactive (colloidal) phase consists of microscopic particles that react with the liquid and consists mainly of clays. The other solid phase, the non-reactive phase, consists of finely ground solids such as sand, chert, limestone and some shales [52]. This non- reactive solid are undesirable due to their abrasive nature on rig equipment and reactive solids could be an issue if they cause distortion of the viscous properties of the mud making them non-reusable. The particle sizes of the solids of this reactive phase (colloids) range from 0.005 – 1 micron and the solids of the non reactive phase range from 1-50 microns for silt and barite and 50-420 microns for sand [53].

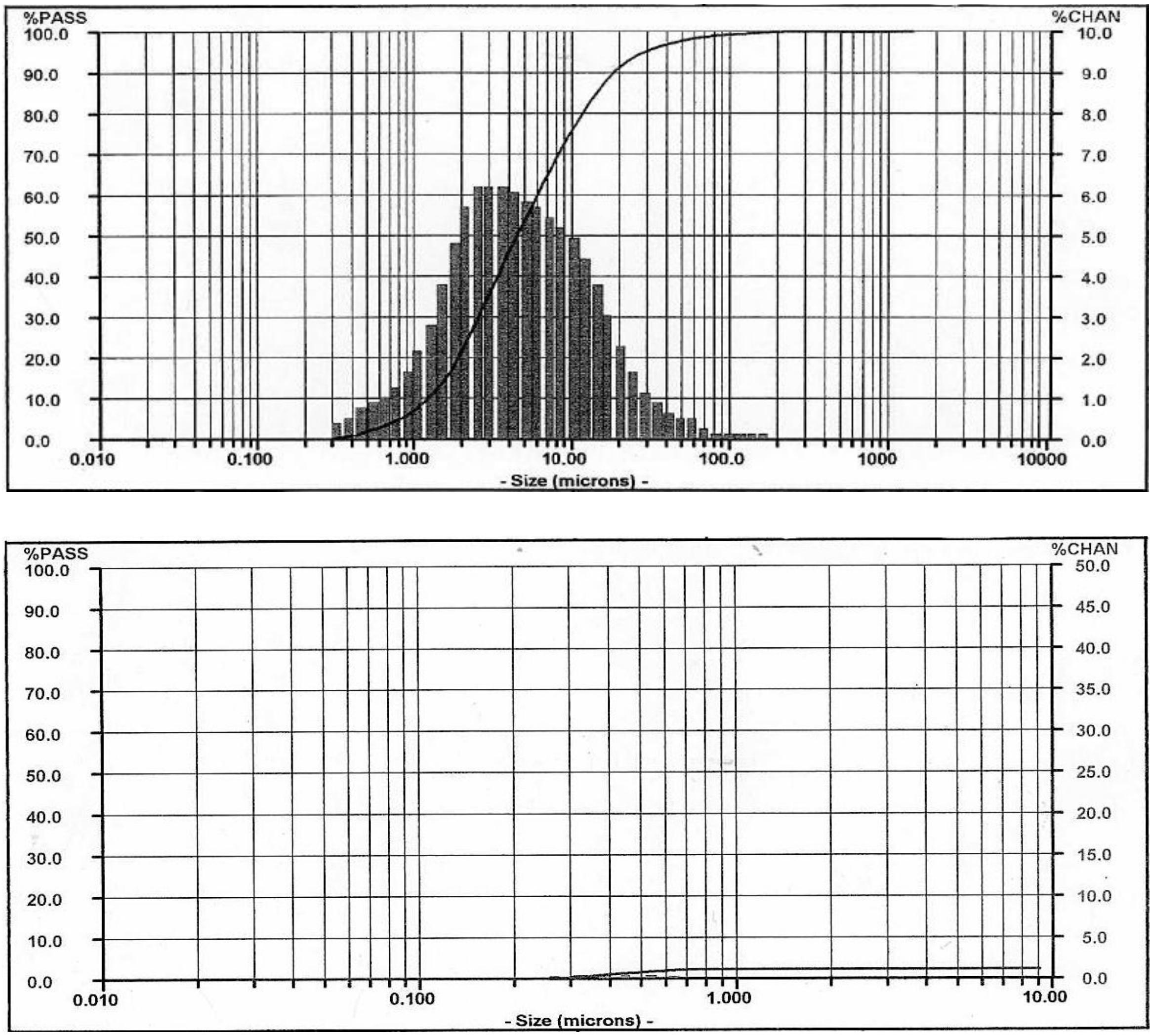


Fig. 3. 2 Shows the particle size distribution of the spent drilling fluid sample filtered using the ceramic. Top is the feed particle size distribution while the bottom is for the permeate.

From figure 3.2 the feed with 8.8± 0.5% vol volume solids has a particle size distribution of solids from between 0.3 microns to 100 microns with mean particle size distribution at 55 microns and median particle size at 11.35 microns. After filtration the permeate particle size distribution is seen to be less than 1 micron and at the threshold limits of particle size analyzer thus it was hard to get a repeatable solids distribution. Using turbidity values the turbidity of feed was 1652 NTU and the permeate turbidity at all points was less than 1.16 NTU. These values of the effluent quality exceed the requirement in particle size distribution needed for re-use purposes in oil field applications

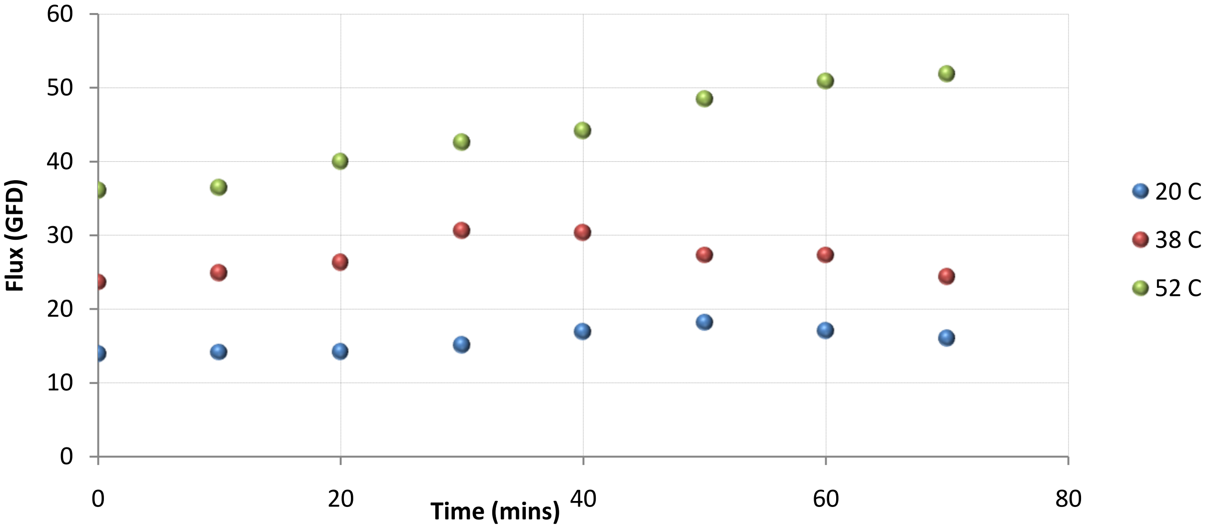


Fig. 3. 3 Temperature variation in the ceramic filtration of spent drilling. Solids concentration (8.8± 0.5% vol) and pH (9.5). Ceramic membrane pore size (0.005 micron), transmembrane pressure (15 psi), cross flow velocity (10.08 ft/s) and temperatures (20 C, 38 C and 52 C).

Temperature in the filtration of the spent drilling fluid was varied from 20 C to 52 C while holding all the other operating parameters constant (transmembrane pressure = 15 psi, cross flow velocity =10.08 ft/s). In the ceramic filtration of the spent drilling fluid at 20 C, the average flux was 15.65 gallons per foot square per day (GFD), maximum permeate flux was 18.14 GFD and the lowest flux was 13.89 GFD, see figure 3.3. Flux decline for the experiment period was less than 20% of the highest recorded flux and there was no significant pressure increase. There was 96% rejection of the solids by the membrane as the feed solids concentration and permeate solids concentration was 21070 mg/L and 856mg/L respectively. The volume concentration factor was 1.18 and the volume reduction was 0.84 i.e. the final volume was 84 % of the initial volume. Filtration for this duration and at these condition extracted 16% of the feed for reuse.

In the ceramic filtration of the spent drilling fluid at 52 C, the average flux was 43.77 gallons per foot square per day (GFD), maximum permeate flux was 51.84 GFD and the lowest flux was 36.1 GFD. Flux decline for the experiment period was also less than 20% of the highest recorded flux and there was no significant pressure increase. There was 95% rejection of the solids by the membrane as the feed solids concentration and permeate solids concentration was 19,354 mg/L and 864 mg/L respectively. The volume concentration factor was 1.74 and the volume reduction was 0.572 i.e. the final volume was 57 % of the initial volume. Filtration for this duration and at these condition extracted 42% of the feed for reuse. The values for the results of filtration at 38 C are reported above.

Table 3.1 Flux characteristics of temperature variation in the ceramic filtration of spent drilling fluids

Temperature	Max Flux (GFD)	Min Flux (GFD)	Average Flux (GFD)	Total Permeate (gal)
20 C	18.14	13.89	15.65	1.22
38 C	30.57	26.31	26.80	2.09
52 C	51.84	36.10	43.77	3.42

By increasing the temperature by 22 C the average flux and total extractable permeate all increased by about 40%, see table 3.1. Temperature increase has been reported to increase flux in the absence of anomalies such as chemical precipitation. Temperature generally reduces the viscosity and fluid density of the feed sample, this allows for more flow of the permeate through the pores. Diffusion coefficient is an increasing function of temperature generally increasing by 3-3.5% for every degree increase thereby allowing greater permeation [52]. With increased temperature resulting in reduced viscosity more of the material is passed through the membrane and in practical terms temperature increase of about 30-45 C is believed to double the flux [40]. Costs are also significantly reduced. In the processing of whey milk operating at a higher temperature reduces the viscosity by 50% and reduced the overall pumping costs creating an annual savings of about 40% in a for a 30 C temperature difference [59].

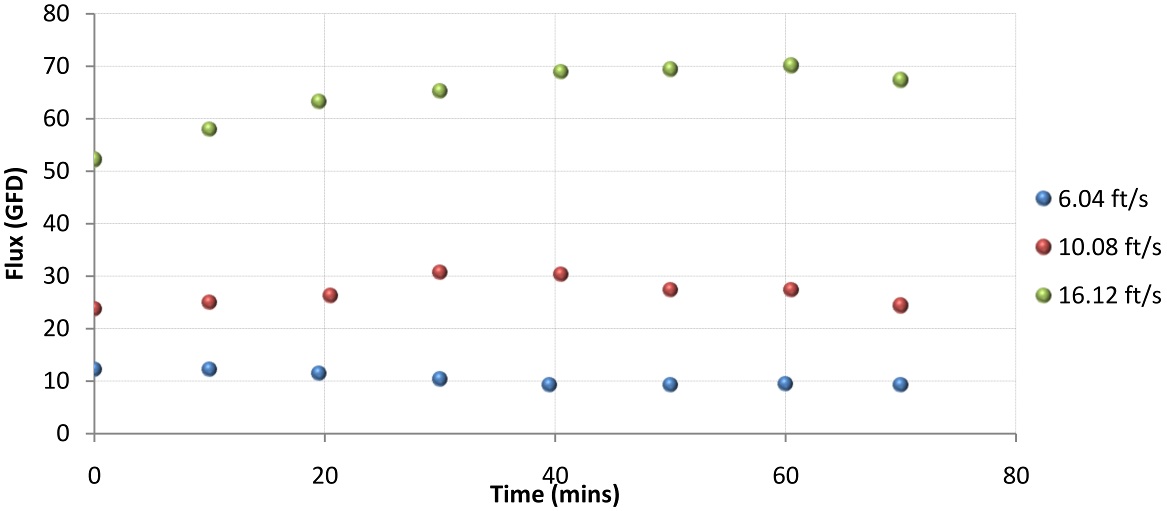


Fig. 3. 4 Cross flow variation in the ceramic filtration of spent drilling. Solids concentration (8.8 ± 0.5% vol) and pH (9.5). Ceramic membrane pore size (0.005 micron), transmembrane pressure (15 psi), cross flow velocity (6.04 ft/s, 10.08 ft/s and 16.12 ft/s) and temperature (38 C).

Cross flow variation in the filtration of the spent drilling fluid using ceramic membrane was varied from 6.04 ft/s to 16.12 ft/s corresponding to 6 gpm to 16 gpm, while holding all the other operating parameters constant (transmembrane pressure = 15 psi, Temperature =38 C). In the ceramic filtration of the spent drilling fluid at 6.04 ft/s, the average flux was 10.36 gallons per foot square per day (GFD), maximum permeate flux was 12.17 GFD and the lowest flux was 9.2 GFD, see figure 3.4. Flux decline for the experiment period was also less than 25% of the highest recorded flux and there was no significant pressure increase. There was 95% rejection of the solids by the membrane as the feed solids concentration and permeate solids concentration was 24361 mg/L and y 1112 mg/L respectively. The volume concentration factor was 1.11 and the volume reduction was 0.89 i.e. the final volume was 89 % of the initial volume. Filtration for this duration and at these condition extracted 11% of the feed for reuse.

In the ceramic filtration of the spent drilling fluid at 16.12 ft/s, the average flux was 64.23 gallons per foot square per day (GFD), maximum permeate flux was 70.07 GFD and the lowest flux was 52.13 GFD. Flux decline for the experiment period was also less than 20% of the highest recorded flux and there was no significant pressure increase. There was 96% rejection of the solids by the membrane as the feed solids concentration and permeate solids concentration was 19,074 mg/L and 733 mg/L respectively. The volume concentration factor was 2.67 and the volume reduction was 0.37 i.e. the final volume was 37 % of the initial volume. Filtration for this duration and at these condition extracted 62% of the feed for reuse. The values for the results of filtration at 10.08 ft/s are reported above.

Table 3.2 Flux characteristics of cross flow variation in the ceramic filtration of spent drilling fluids. CFV=cross flow velocity

CFV (ft/s)	Max Flux (GFD)	Min Flux (GFD)	Average Flux (GFD)	Total Permeate (gal)
6	12.17	9.2	10.36	0.81
10.08	30.57	26.31	26.80	2.09
16	70.07	52.13	64.23	5.01

Cross flow filtration involves the flow of the feed tangentially to the membrane surface, there is one stream entering into the membrane and two streams flowing out of the membranes, the permeate stream flows perpendicular to the inlet flow and the retentate flows in the same plane as the feed. Cross flow filtration affects flux decline because it can be used to control concentration polarization especially with feeds that have high solids content [40,60,63]. The flow regimen in the ceramic filtration of spent drilling fluid is turbulent, at 6.04 ft/s, 10.08 ft/s and 16.12 ft/s the Reynolds number were 5762.88 9521.28 and 15388.90 respectively. The turbulence produced by the flow “scours” the membrane surface due to the shear removing the accumulated solids from the membrane surface and reducing the hydraulic resistance of the concentration polarization layer reducing the cake thickness.

At higher cross flow velocities it is observed that flux rate increases, total permeate increased by 100% when the cross flow velocity was increased by 6 ft/s in the ceramic filtration of spent drilling mud, see table 3.2. The turbulence at 16.12 ft/s was effective in controlling the concentration polarization layer and due to the higher flow rate more feed is also processed through the membrane. The shearing action of the flow makes the membrane surface layer “dynamic” as the solids concentration of the spent drilling mud acts to brush the surface.

Increasing cross flow velocity does not always guarantee higher fluxes especially in the pressure controlled region if the solids concentration is too low [40]. Particle size distribution is also seen to affect cross flow velocity effect on flux, Wakeman and Tarleton [60] show that in the filtration of a feed with ground calcite, flux reduced with higher cross flow velocities when the mean particle size of the feed was increased.

Increased cross flow velocity means in practical terms means higher pump energy and higher operational costs in membrane filtration of wastes. The benefits of increasing the cross flow velocity is usually weighed with the cost benefit of increased permeate volume or flux. Pressure regimen at high cross flow velocities is important as pressures contribute significantly to resistances during high cross flow velocity. Using higher cross flow velocities at low pressure regimens would delay the onset of fouling significantly but this advantage has to be weighed with respect to the volume of permeate generated. Low pressures would not generate high permeate volumes relative to permeate volumes at high pressure. Combinations of high cross flow velocity and high temperature would favorably increase permeate flux in a high solids feed as spent drilling fluids.

As would be explained in the discussion on transmembrane pressure variation, during filtration flux equilibrates at the point where convective transportation of the solids to the surface equals the rate of back diffusion of the solids from the membrane surface. High cross flow velocities cause the scouring of the membrane surface but at high pressures the layer at the membrane surface is consolidated. There becomes a time where at increased cross flow velocity and high pressure there is no gain in permeate volume as the solids consolidation at the surface prevents their removal, this is the reason why pressure regimens are important at high cross flow velocities [40,49].

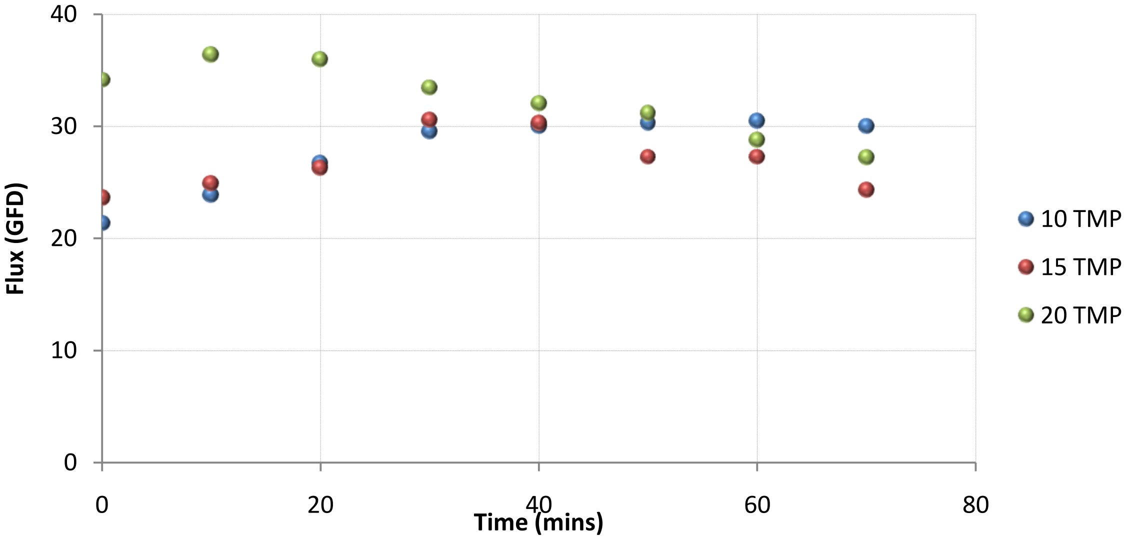


Fig. 3. 5 Transmembrane pressure variation in the ceramic filtration of spent drilling. Solids concentration (8.8± 0.5% vol) and pH (9.5). Ceramic membrane pore size (0.005 micron), transmembrane pressure (10, 15 and 20 psi), cross flow velocity (10.08 ft/s) and temperature (38 C).

Transmembrane pressure variation in the filtration of the spent drilling fluid using ceramic membrane was varied from 10 psi to 20 psi while holding all other operating parameters constant (cross flow velocity =10.08 ft/s, Temperature =38 C). In the ceramic filtration of the spent drilling fluid at transmembrane pressure of 10 psi, the average flux was 27.85 gallons per foot square per day (GFD), maximum permeate flux was 30.47 GFD and the lowest flux was 21.35 GFD, see figure 3.5. Flux decline for the experiment period was also less than 15% of the highest recorded flux and there was no significant pressure increase. There was 95% rejection of the solids by the membrane as the feed solids concentration and permeate solids concentration was 22785 mg/L and 1165 mg/L respectively. The volume concentration factor was 1.37 and the volume reduction was 0.72 i.e. the final volume was 72 % of the initial volume. Filtration for this duration and at these condition extracted 28% of the feed for reuse.

In the ceramic filtration of the spent drilling fluid at transmembrane pressure of 20 psi, the average flux was 32.38 gallons per foot square per day (GFD), maximum permeate flux was 34.11 GFD and the lowest flux was 27.22 GFD. Flux decline for the experiment period dropped rapidly by about 20% of the highest flux. There was 97% rejection of the solids by the membrane as the feed solids concentration and permeate solids concentration was 21,147 mg/L and 916 mg/L respectively. The volume concentration factor was 1.46 and the volume reduction was 0.68 i.e. the final volume was 68 % of the initial volume. Filtration for this duration and at these condition extracted 32% of the feed for reuse. The values for the results of filtration at 15 psi are reported above.

Table 3.3 Flux characteristics of transmembrane pressure variation in the ceramic filtration of spent drilling fluids. TMP=transmembrane pressure

TMP (psi)	Max Flux (GFD)	Min Flux (GFD)	Average Flux (GFD)	Total Permeate (gal)
10	21.35	30.47	27.85	0.81
15	30.57	26.31	26.80	2.09
20	34.11	27.22	32.38	5.01

In the pressure controlled region i.e. when there is a low feed concentration, high cross flow velocity and low pressure regimen it is seen that flux increases with pressure linearly (see chapter II). In the mass controlled region where we have high feed concentration such as in spent drilling mud and medium to high cross flow velocities and pressure the dynamics of filtration in markedly different. In this condition the effect on the concentration polarization layer is a reverse of the scouring seen at high cross flow velocities rather there is a consolidation of the concentration polarization layer due to the effect of pressure on filtration causing an increase in hydraulic resistance hastening, the onset of flux reduction. Table 3.3 gives a summary of the fluxes.

As seen in Figure 3.5 where pressure is varied, at 20 psi transmembrane pressure there is an onset of increased flux but after 20 minutes the flux starts to decline rather rapidly. This phenomenon is believed to be due to the consolidation of the concentration polarization layer as observed by Altmann and Ripperger [61]. Convective transport brings solid particles to the membrane surface and a steep concentration gradient develops within the boundary layer, at the same time back transport of the solids occurs due to diffusion. A steady state is soon reached where the convective transport of solids to the membrane surface is balanced by the diffusion back transport of the solids into the bulk. There arises a point where the solute buildup at the membrane surface is saturated i.e. the close packed arrangement of the solids at the membrane surface, at this point additional pressure forces the solids at the membrane surface to squeeze into pore spaces thereby fouling the membranes. At this point operation parameters such as increasing cross flow velocity have no effect on permeate flux.

At 20 psi at a cross flow velocity of 10.08 ft/s the dense close arrangement at the wall seems to build up rapidly, there is an initial increased permeate flow due to the pressure and this would account for more materials reaching the surface of the membrane. At the same cross flow velocity, increasing membrane resistance is observed starting from about 25 minutes, the transmembrane pressure rises by about 3 psi from that moment till the end of filtration indicating fouling and the minimum flux drops below the minimum flux at 10 psi. At the lower transmembrane pressure of 10 psi the reverse is noted, the equilibrium state between the convective and diffusion forces in the transport of the solids takes a longer time, this is evidenced by the increasing flux with time, at about 40 minutes at 15 psi flux decline is setting in and till the end of the experiment at transmembrane pressure of 10 psi no appreciable decline occurs.

Essential to filtration optimization is the balance between the operational parameters especially cross flow velocity and transmembrane pressure, if not properly managed they would accelerate the onset of fouling. High cross flow velocities increase permeation at low pressures for most feeds; Wakeman and Tarleton [60] describe the “tubular pinch” to explain the decrease in flux with increasing high cross flow velocities, a situation where progressively fine particles are deposited on the membrane surface as the larger particles remain in suspension. Higher transmembrane pressures at high cross flow velocities would accelerate the deposition of the finer particles on the membrane surface.

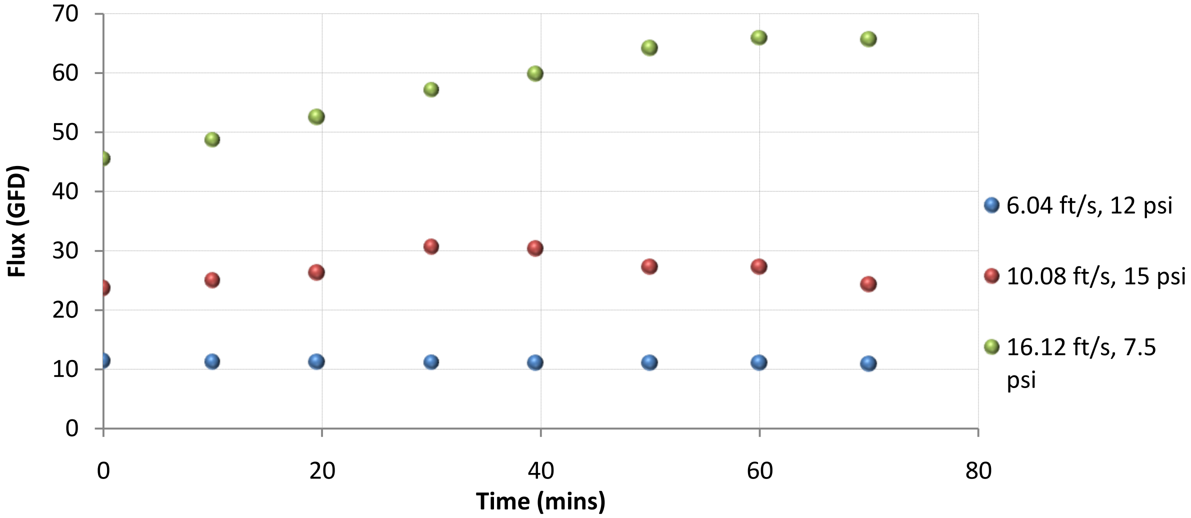


Fig. 3. 6 Varied parameters ceramic filtration of spent drilling. Solids concentration (8.8± 0.5% vol) and pH (9.5). Ceramic membrane pore size (0.005 micron), transmembrane pressure (7.5, 12 and 15 psi), cross flow velocity (6.04,10.08 and 16.12 ft/s) and temperature (38 C).

A mixed regimen of the operational parameters was carried out. A regimen with medium transmembrane with low cross flow velocity (cross flow velocity =6.04 ft/s, transmembrane pressure = 12 psi) and another with a high cross flow velocity and low pressure (cross flow velocity =16.12 ft/s, transmembrane pressure = 7.5 psi) were investigated. In the ceramic filtration of the spent drilling fluid at cross flow velocity of 6.04 ft/s and transmembrane pressure of 12 psi, the average flux was 11.07 gallons per foot square per day (GFD), maximum permeate flux was 11.38 GFD and the lowest flux was 10.85 GFD, see figure 3.6. Flux decline for the experiment period was also less than 8% of the highest recorded flux and there was no significant pressure increase. There was 95% rejection of the solid by the membrane as the feed solids concentration and permeate solids concentration was 19,147 mg/L and 1016 mg/L respectively. The volume concentration factor was 1.10 and the volume reduction was 0.90 i.e. the final volume was 90% of the initial volume. Filtration for this duration and at these condition extracted 9% of the feed for reuse.

In the ceramic filtration of the spent drilling fluid at cross flow velocity of 16.12 ft/s and transmembrane pressure of 7.5 psi, the average flux was 57.39 gallons per foot square per day (GFD), maximum permeate flux was 65.85 GFD and the lowest flux was 45.45 GFD. Flux decline for the experiment period was also less than 20% of the highest recorded flux and there was no significant pressure increase. There was 94% rejection of the solids by the membrane as the feed solids concentration and permeate solids concentration was 16,332mg/L and 963 mg/L respectively. The volume concentration factor was 2.27 and the volume reduction was 0.44 i.e. the final volume was 44% of the initial volume. Filtration for this duration and at these condition extracted 55% of the feed for reuse.

Table 3. 4 Varied parameter variation in the ceramic filtration of spent drilling fluids. TMP=transmembrane pressure, CFV= cross flow velocity

CFV (ft/s), TMP (psi)	Max Flux (GFD)	Min Flux (GFD)	Average Flux (GFD)	Total Permeate (gal)
6.04, 12	11.38	10.85	11.07	2.17
10.08, 15	30.57	26.31	26.80	2.09
16.12, 7.5	68.85	45.45	57.39	2.53

In this mixed regimen filtration we see that by lowering the transmembrane pressure and using high cross flow velocity the onset of the flux decline is prolonged though the total permeate volume is less than the situation with high cross flow velocity and medium transmembrane pressure. This reduced permeate volume is due to the difference in transmembrane pressures from 15 psi and 7.5 psi. It is also observed that when low cross flow velocity is used with medium transmembrane pressure we have stable flux and no discernable flux decline throughout the experiment duration. This regimen comparison shows the operational balance needed in effectively maintaining flux during filtration of any waste stream. Table 3.4 gives a summary of the fluxes.

3.2.2 Drilling Fluid Solids Concentration Variation

The solids concentration of the drilling fluid sample was varied to determine what the effect would be on filtration using the ceramic membrane. To prepare a more concentrated sample than the feed delivered from the field the retentate of previous filtration was mixed with fresh feed and the solids concentration determined. A 10.2 % vol solids concentration feed was prepared using the retentate from previous spent drilling filtration experiments. A more dilute solution than the initial feed solids concentration was not prepared.

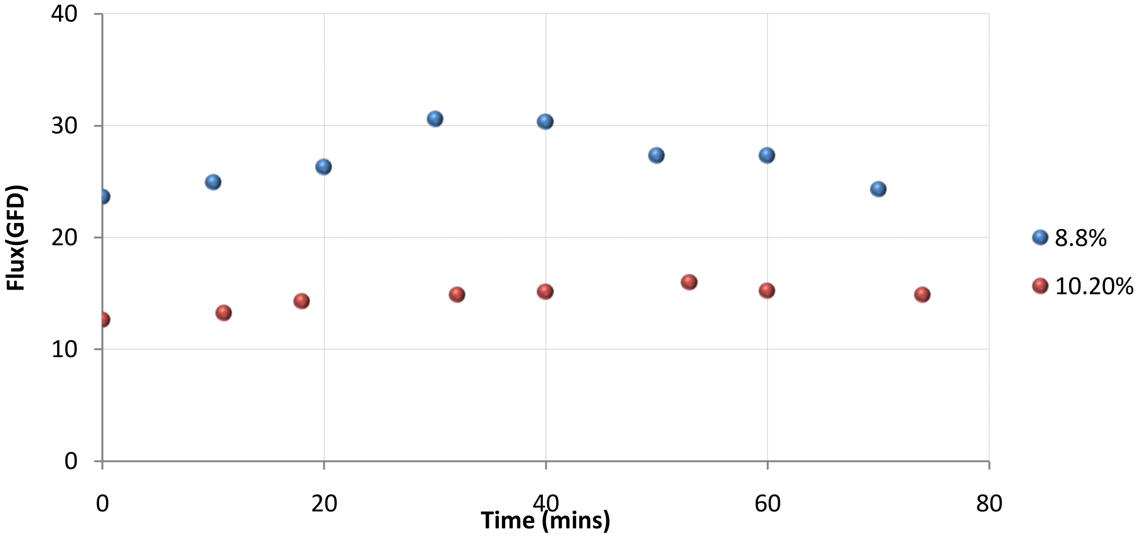


Fig. 3. 7 Solids concentration variation in the ceramic filtration of spent drilling. Solids concentration (8.8± 0.5% and 10.20± 0.15% vol) and pH (9.5). Ceramic membrane pore size (0.005 micron), transmembrane pressure (15 psi), cross flow velocity (10.08 ft/s) and temperature (38 C).

Solids concentration variation in the filtration of the spent drilling fluid using ceramic membrane was varied from 8.8± 0.5% and 10.20± 0.15 % volume while holding all other operating parameters constant (cross flow velocity =10.08 ft/s, Temperature =38 C). In the ceramic filtration of the spent drilling fluid at transmembrane pressure of 8.8± 0.5%, the average flux was 26.8 gallons per foot square per day (GFD), maximum permeate flux was 30.57 GFD and the lowest flux was 26.31 GFD, see figure 3.7. Flux decline for the experiment period was less than 20% of the highest recorded flux and there was no significant pressure increase during the experiment. There was 95 % rejection of the solids by the membrane as the feed solids concentration and permeate solids concentration was 18061 mg/L and 774 mg/L respectively. The volume concentration factor was 1.33 and the volume reduction was 0.75 i.e. the final volume was 75 % of the initial volume. Filtration for this duration and at these condition extracted 25% of the feed for reuse i.e. clean useable effluent for oil-field uses was 25% of the initial waste volume.

In the ceramic filtration of the spent drilling fluid at transmembrane pressure of 10.20 ± 0.15% the average flux was 14.5 gallons per foot square per day (GFD), maximum permeate flux was 15.99 GFD and the lowest flux was 12.6 GFD. Flux decline for the experiment period was less than 12% of the highest recorded flux and there was no significant pressure increase during the experiment. There was 90% rejection of the solids by the membrane as the feed solids concentration and permeate solids concentration was 33718 mg/L and 3064mg/L respectively. The volume concentration factor was 1.16 and the volume reduction was 0.85 i.e. the final volume was 85 % of the initial volume. Filtration for this duration and at these condition extracted 14% of the feed for reuse i.e. clean useable effluent for oil-field uses was 14% of the initial waste volume.

Table 3.5 Solids concentration variation in the ceramic filtration of spent drilling fluids. conc. = concentration

Solids conc. % vol	Max Flux (GFD)	Min Flux (GFD)	Average Flux (GFD)	Total Permeate (gal)
8.8 ± 0.5	30.57	26.31	26.80	2.09
10.20 ± 0.15	15.99	12.62	14.52	1.13

At higher solids concentration the average flux is about 50% lower than the flux at the lower solids concentration. High solids concentration results in high feed viscosity thus more energy is required to pump the feed through the membrane. At the same filtration conditions the feed with the higher solids concentration has more solids particles and thus the probability for flux decline is higher though the decline was not very steep in this case. The observable hump in filtration when filtering drilling mud is not observed when the solids concentration was increased; this might be because the saturation of the solids on the membrane surface occurs quickly. Flux remains fairly normal during filtration and this might be the base flux achievable under the filtration conditions. Viscosity and solids concentration are the dominant factor at higher solids concentration. Though there are reports in literature of filtering with about 20% solids, the flux and the possibility of abrasion of spent drilling fluid solids on the membrane makes filtering such high concentration seem impractical. Table 3.5 gives a summary of the fluxes.

3.3 Produced Water Filtration with Ceramic Membrane

3.3.1 Parameter Variation in Produced Water Ceramic Filtration

Feed samples for filtration of produced water were procured directly from disposal trucks from the field. Using portable kits concentrations of the oil in water, salinity and some dissolved solids were carried out to see if the feed was within the specified arbitrary range. The feed parameter of interest in the filtration of produced water was primarily oil in water concentration and turbidity. The arbitrary produced water was defined to have an oil concentration range of 250 – 1200 ppm oil in water, turbidity of less than 4000 NTU, pH of 6.5 – 10 and TDS less than 40,000 ppm. The initial feed volume was 10 gallons for normal filtration experiments. Arbitrary operating parameters for ceramic filtration was a cross flow velocity of 8 ft/s, transmembrane pressure of 15 psi and temperature of 38 C. Temperature was varied between 20 and 52 C, transmembrane pressure varied between 10 and 21 psi and cross flow velocity varied between 4 and 11 ft/s. The feed parameter of interest the oil concentration was varied between 200 and 1200 ppm. The objective of produced water ceramic filtration is to serve as a mechanical pre-treatment of the produced water for removal of oil and turbidity (suspended solids).

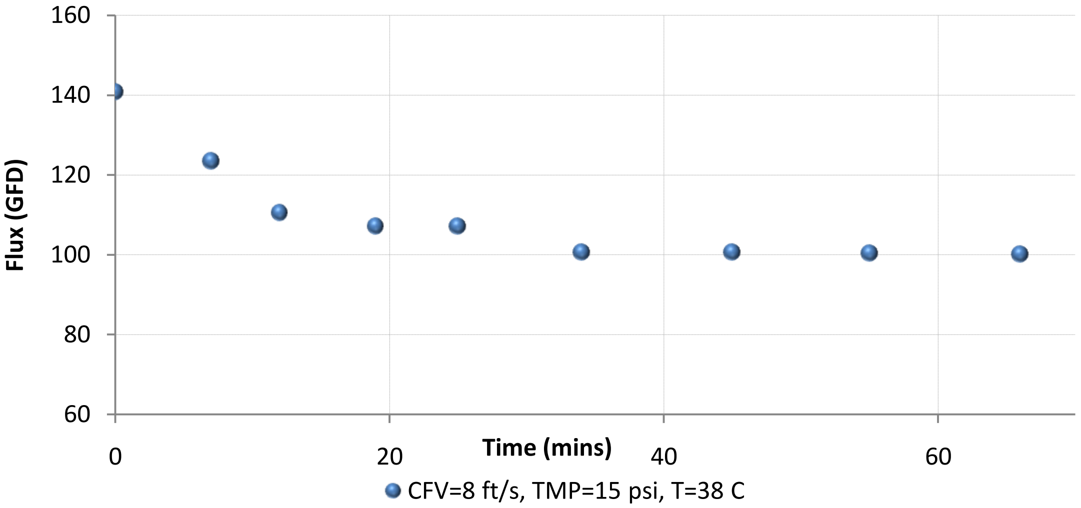


Fig. 3. 8 Ceramic filtration of produced water. Oil concentration 700± 500 ppm, pH 7.3± 1.5 and salinity 36,000± 5000 TDS mg/L. Ceramic membrane pore size (0.005 micron), transmembrane pressure (15 psi), cross flow velocity (8 ft/s) and temperature (38 C).

In the ceramic filtration of produced water with oil concentration 700± 500 ppm, pH 7.3± 1.5 and salinity 36,000± 5000 TDS mg/L filtering at a transmembrane pressure of 15 psi, cross flow velocity of 8 ft/s (corresponding to 8 gallons per minute (gpm)) and temperature of 38 C, the average flux was 110.06 gallons per foot square per day (GFD), maximum permeate flux was 140.7 GFD and the lowest flux was 100.11 GFD, see figure 3.8. Flux decline for the experiment period was about 40% of the highest flux and there was no significant pressure increase. Unlike spent drilling fluid where the concentration of the solids in the feed is important the particle size distribution and sizes are much lower with the median particle size and concentration being 75 microns and 24 microns respectively. Solids rejection was 99% in all cases and turbidity reduction was also 99% in all cases, permeate turbidity at all points was less than 1 NTU. There was 99% rejection of the oil as the feed concentration and permeate concentration was 913 mg/L and 5 mg/L respectively. The volume concentration factor was 4.36 and the volume reduction was 0.23 i.e. the final volume was 23 % of the initial volume. Filtration for this duration and at these condition extracted 77% of the feed as effluent.

Produced water filtration is markedly different from spent drilling fluids as the viscosity, solids concentration and oil content differ significantly. The viscosity of the produced water is less than the viscosity of spent drilling fluids, the solids concentration is also lower and the oil content in produced water is higher than that of spent drilling fluids. The filtration dynamics of produced water differs markedly because the oil concentration and not the solids is believed to be the dominant feed characteristic causing resistance to filtration. In the filtration of oily wastes waters, different authors explain the mechanism of flux resistance in varied ways. One of which is that oil droplets coalesce onto the surface of the membrane creating a gel-polarized layer that creates resistance to filtration [62] while another mechanism is believed to start with internal fouling of the membrane pores (pore blocking) and then an external layer formation (gel layer) [63].

In the filtration of produced water using ceramic membranes there is a rapid flux decline initially between the first 20 minutes of filtration, after this period the flux equilibrates at about thirty minutes and remains constant for the duration of filtration. This rapid flux decline could be due to adsorption of the oil droplets on the membrane surface, pore plugging or formation of a gel layer. Though the mechanism is not ascertained, the role of solids in fouling is limited. Mueller et al [62] showed that the presence of solids helped to enhance flux as the solids act as a dynamic membrane layer preventing oil from fouling the membrane internally and they help to absorb the oil droplet and break up the continuous coalesced oil cake layer. Oil droplets can also plug the pores of the membranes. If the mechanism of pore plugging explains the flux decline, as filtration occurs oil droplets are squeezed into pore spaces constricting the flow of the permeate, the flux equilibrium is achieved at the saturation of the oil concentration/solids in the pore. If a gel concentration theory explains the mechanism of flux decline as filtration occurs oil droplets start to form a layer at the membrane surface and flux equilibrium is achieved when the wall is saturated.

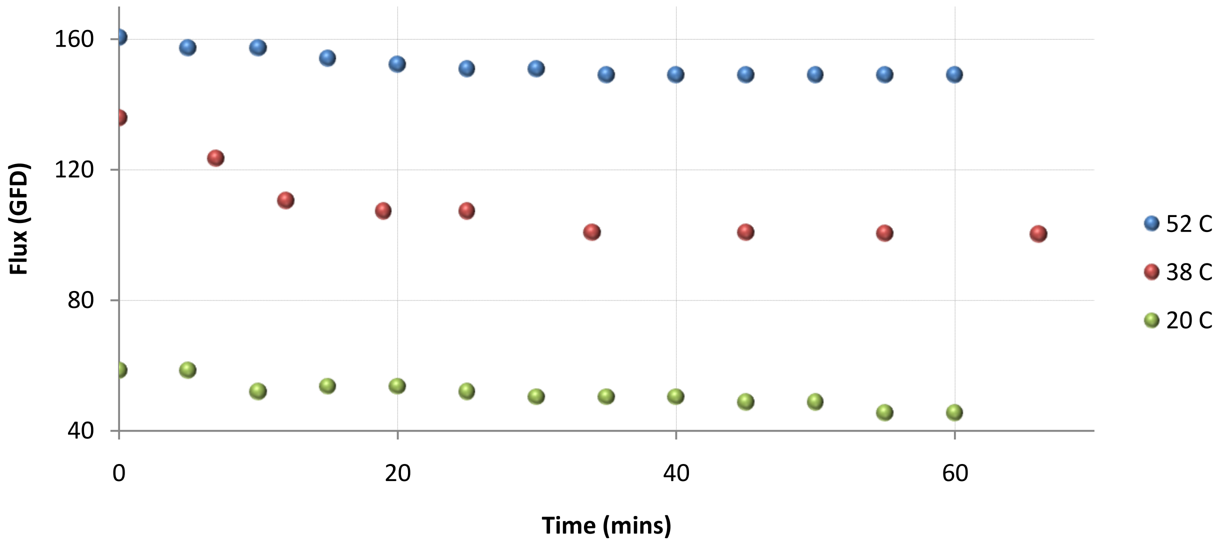


Fig. 3. 9 Temperature variation in the ceramic filtration of produced water. Oil concentration 700± 500 ppm, pH 7.3± 1.5 and salinity 36,000± 5000 TDS mg/L.. Ceramic membrane pore size (0.005 micron), transmembrane pressure (15 psi), cross flow velocity (8 ft/s) and temperature (20,38 and 52 C).

In the ceramic filtration of produced water oil concentration 700± 500 ppm, pH 7.3± 1.5 and salinity 36,000± 5000 TDS mg/L filtering at a transmembrane pressure of 15 psi, cross flow velocity of 8 ft/s and temperature of 20 C, the average flux was 51.32 gallons per foot square per day (GFD), maximum permeate flux was 58.44 GFD and the lowest flux was 45.45 GFD, see figure 3.9. Flux decline for the experiment period was about 46% of the highest flux and there was no significant pressure increase. Solids rejection was 99% in all cases and turbidity reduction was also 99% in all cases and permeate turbidity was less that 1 NTU. There was 98% rejection of the oil in water concentration by the membranes as the feed concentration and permeate concentration was 694 mg/L and < 1 mg/L respectively. The volume concentration factor was 1.48 and the volume reduction was 0.67 i.e. the final volume was 67 % of the initial volume. Filtration for this duration and at these condition extracted 32% of the feed as effluent.

In the ceramic filtration of produced water oil concentration 700± 500 ppm, pH 7.3± 1.5 and salinity 36,000± 5000 TDS mg/L filtering at a transmembrane pressure of 15 psi, cross flow velocity of 8 ft/s and temperature of 52 C, the average flux was 152.05 gallons per foot square per day (GFD), maximum permeate flux was 160.40 GFD and the lowest flux was 149.01 GFD. Flux decline for the experiment period was about 7% of the highest flux and there was no significant pressure increase. There was 99 % rejection of the oil in water concentration by the membranes as the feed concentration and permeate concentration was 761 mg/L and 2 mg/L respectively. The volume concentration factor was 27.77 and the volume reduction was 0.04 i.e. the final volume was 4% of the initial volume. Filtration for this duration and at these condition extracted 95% as effluent. The values for the results of filtration at 38 C are reported on page above.

Table 3.6 Flux characteristics of temperature variation in the ceramic filtration of produced water

Temperature (C)	Max Flux (GFD)	Min Flux (GFD)	Average Flux (GFD)	Total Permeate (gal)
20 C	58.44	45.45	51.32	3.52
38 C	140.70	100.11	110.06	7.71
52 C	160.04	149.01	152.05	9.64

Temperature had the same effect on filtration as noticed during the filtration of spent drilling mud i.e. as the temperature increased the flux also increased. The temperature reduces the viscosity of the feed sample and thus with increasing temperature the viscosity is lower and the flux higher. Increasing temperature is known to also reduce viscosity of the oil, this would allow the flow of more oil through the pores prolonging the onset of fouling and reducing the hydraulic resistance to the flow of permeate. The oil content in the permeate was not statistically higher than the permeate under the increased temperature operations.

Using the flux values, it seems the flux doubles with every 16 degree rise in temperature though the difference in flux between the 20 and 38 C is slightly less proportionate to the difference between 38 and 52 C. Low temperature would not only increase the feed viscosity alone but would also affect the nature (viscosity) of the oil, this might accelerate the formation of a gel layer on the membrane surface creating resistance to flow of the permeate. With increasing temperature we also see a delay in flux decline, at 52 C we see that flux decline was just less than 7% of the highest recorded flux compared to 46% at 20 C. Increasing temperature is not only beneficial at increasing the permeate volume it is also beneficial at prolonging the onset of flux decline. Table 3.6 gives a summary of the fluxes.

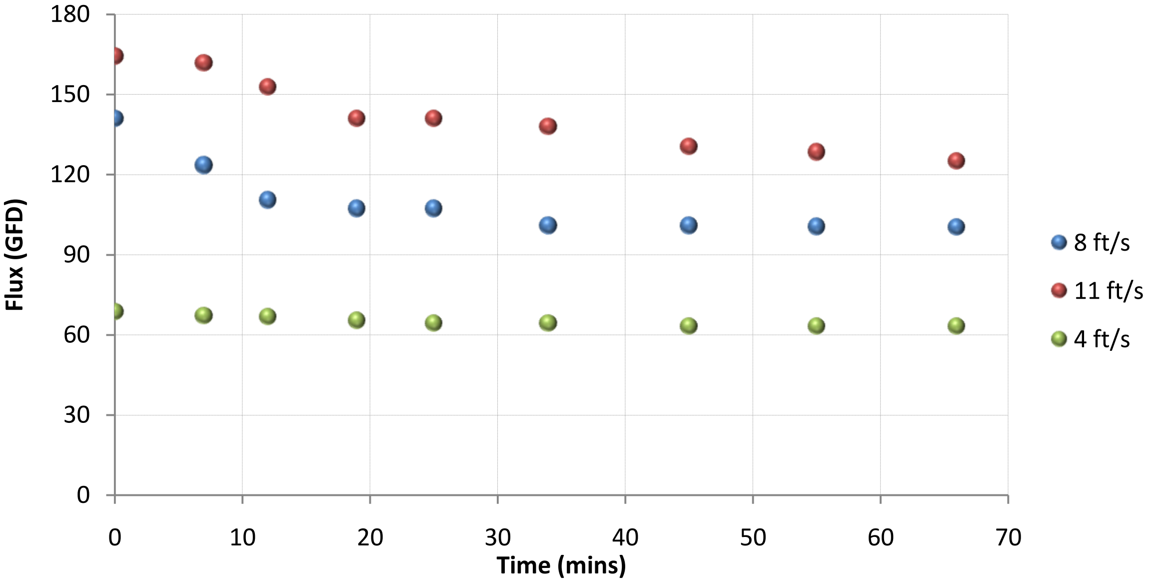


Fig. 3. 10 Cross flow velocity variation in the ceramic filtration of produced water. Oil concentration 700± 500 ppm, pH 7.3± 1.5 and salinity 36,000± 5000 TDS mg/L.. Ceramic membrane pore size (0.005 micron), transmembrane pressure (15 psi), cross flow velocity (4,8 and 11 ft/s) and temperature (38 C).

In the ceramic filtration of produced water oil concentration 700± 500 ppm, pH 7.3± 1.5 and salinity 36,000± 5000 TDS mg/L filtering at a transmembrane pressure of 15 psi, cross flow velocity of 4 ft/s and temperature of 38 C, the average flux was 65.03 gallons per foot square per day (GFD), maximum permeate flux was 68.42 GFD and the lowest flux was 63.10 GFD, see figure 3.10. Flux decline for the experiment period was about 8% of the highest flux and there was no significant pressure increase. Solids rejection was 99% in all cases and turbidity reduction was also 99% all permeate samples had less than 1 NTU. There was 98% rejection of the oil in water concentration by the membranes as the feed concentration and permeate concentration was 1104 mg/L and 12 mg/L respectively. The volume concentration factor was 1.85 and the volume reduction was 0.54 i.e. the final volume was 54% of the initial volume. Filtration for this duration and at these condition extracted 45% as effluent.

In the ceramic filtration of produced water oil concentration 700± 500 ppm, pH 7.3± 1.5 and salinity 36,000± 5000 TDS mg/L filtering at a transmembrane pressure of 15 psi, cross flow velocity of 11 ft/s and temperature of 38 C, the average flux was 142.42 gallons per foot square per day (GFD), maximum permeate flux was 164.10 GFD and the lowest flux was 124.8 GFD. Flux decline for the experiment period was about 25% of the highest flux decline and there was no significant pressure increase. There was 99% rejection of the oil in water concentration by the membranes as the feed concentration and permeate concentration was 885 mg/L and < 1 mg/L respectively. Within the experiment duration most of the feed was treated and the concentration volume factor and the volume reduction were close to 100% i.e. most of the feed was treated, more feed had to be added.

Table 3. 7 Flux characteristics of cross flow variation in the ceramic filtration of produced water. CFV=cross flow velocity

CFV (ft/s)	Max Flux (GFD)	Min Flux (GFD)	Average Flux (GFD)	Total Permeate (gal)
4	68.42	63.10	65.03	4.60
8	140.70	100.11	110.06	7.71
11	164.10	124.8	142.42	9.99

With increasing cross flow velocity flux increases though the flux decline profiles at all cross flow velocities are similar. As explained earlier increasing cross flow velocity increases filtration by affecting the wall layer reducing the resistance to permeate flow, this is believed to be the action of the shear caused by flow turbulence aided by the solids in the solution. With a low solids concentration (as in produced water) we see that the impact of increased cross flow velocity is not as dramatic as that of spent drilling fluid filtration as the flux decline profile in produced water filtration remains similar even when velocities are increased. In spent drilling fluids filtration with high solids concentration (Figures 3.4 and 3.6) is it observed that the decline profiles are affected by increasing cross flow velocity as the onset of flux decline is prolonged. Table 3.7 gives a summary of the fluxes.

Shearing action due to turbulence with low solids concentration gives qualified gain from increasing the cross flow velocity. In the presence of increasing oil concentration, it becomes apparent that increasing the cross flow velocity could cease being advantageous as there shall become a point where the fouling dynamics shall overwhelm the shearing action of the flow and cause an acceleration of fouling on the membrane layer or in the pores. As explained earlier increased solids concentration can enhance flux and at higher cross flow velocities or high shear it would be effective at breaking up coalesced oil on the membrane wall.

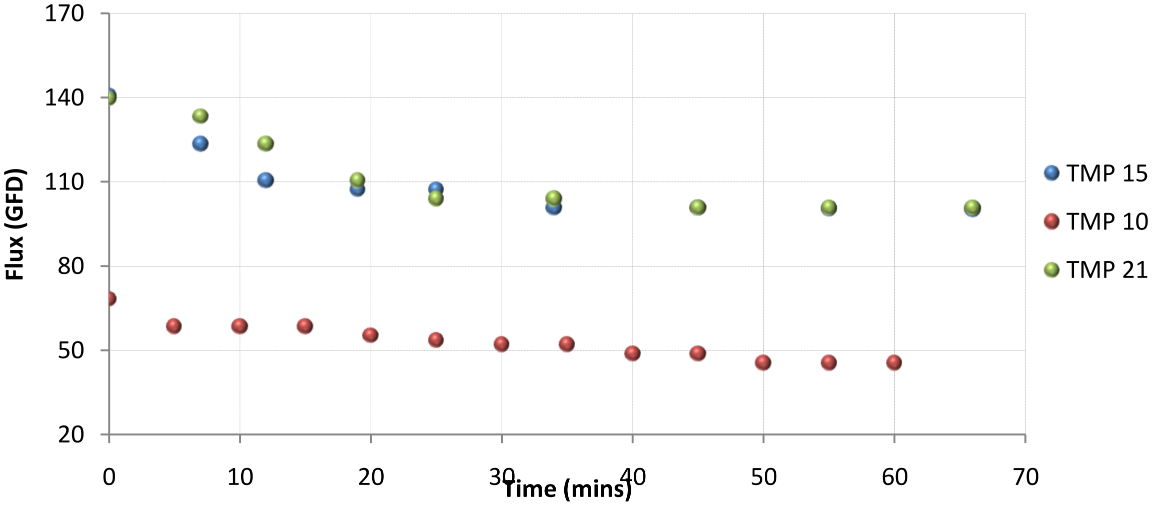


Fig. 3. 11 Transmembrane pressure variation in the ceramic filtration of produced water. Oil concentration 700± 500 ppm, pH 7.3± 1.5 and salinity 36,000± 5000 TDS mg/L. Ceramic membrane pore size (0.005 micron), transmembrane pressure (10, 15 and 20 psi), cross flow velocity (8 ft/s) and temperature (38 C).

In the ceramic filtration of produced water oil concentration 700± 500 ppm, pH 7.3± 1.5 and salinity 36,000± 5000 TDS mg/L filtering at a transmembrane pressure of 10 psi, cross flow velocity of 8 ft/s and temperature of 38 C, the average flux was 53.07 gallons per foot square per day (GFD), maximum permeate flux was 68.18 GFD and the lowest flux was 45.45

GFD, see figure 3.11. Flux decline for the experiment period was about 30% of the highest flux decline and there was no significant pressure increase. Solids rejection was 99% in all cases and turbidity reduction was also 99% in all cases permeate had less than 1 NTU. There was 99% rejection of the oil in water concentration by the membranes as the feed concentration and permeate concentration was 901 mg/L and < 1 mg/L respectively. The volume concentration factor was 1.64 and the volume reduction was 0.61 i.e. the final volume was 61 % of the initial volume. Filtration for this duration and at these condition extracted 38% as effluent.

In the ceramic filtration of produced water oil concentration 700± 500 ppm, pH 7.3± 1.5 and salinity 36,000± 5000 TDS mg/L filtering at a transmembrane pressure of 21 psi, cross flow velocity of 8 ft/s and temperature of 38 C, the average flux was 100.65 gallons per foot square per day (GFD), maximum permeate flux was 139.93 GFD and the lowest flux was 112.00 GFD. Flux decline for the experiment period was about 40% of the highest flux decline and there was significant pressure increase. There was 99% rejection of the oil in water concentration by the membranes as the feed concentration and permeate concentration was 872mg/L and 3 mg/L respectively. The volume concentration factor was 4.72 and the volume reduction was 0.21 i.e. the final volume was 21 % of the initial volume. Filtration for this duration and at these condition extracted 78% as effluent.

Table 3. 8 Flux characteristics of transmembrane pressure variation in the ceramic filtration of produced water. TMP=transmembrane pressure

TMP (psi)	Max Flux (GFD)	Min Flux (GFD)	Average Flux (GFD)	Total Permeate (gal)
10	68.18	45.45	53.07	3.93
15	140.70	100.11	110.06	7.71
21	139.93	112.00	100.65	7.88

Increasing transmembrane pressure increased flux till 20 psi. At 20 psi flux decline is steeper when compared to flux profiles of transmembrane pressures less than 20 psi though the increase in pressure created more permeate volume for the experiment duration. At high pressure the accumulation of oil droplets at the pores or at the membrane surface is accelerated, increasing the resistance to the flow of the permeate. With further increase in pressure the gain in permeate volume would be counterbalanced by high hydraulic resistance caused by increasing consolidation of the concentration polarization layer formed on the wall. It should be noted that membrane flux regeneration after this increased pressure was significantly lower when flushing to clean the membrane. Under this conditions 20 psi seems to be the “threshold pressure” i.e. when the filtration is no longer in the pressure controlled region where increase in the pressure would not bring about a commensurate increase in permeate flow due to the effect of concentration polarization. Table 3.8 gives a summary of the fluxes.

3.3.2. Oil Concentration Variation in the Ceramic Membrane Filtration of Produced Water

The oil concentration in produced water was varied to determine the effect on filtration. To prepare a sample with higher oil in water concentration, crude oil (San Francisco Crude oil 35 API) was added to the sample of produced water and using a laboratory blender was mixed thoroughly. The particle size distribution of the contrived samples was greater than the particle size of the original samples due to the particle size distribution of the oil droplets in the contrived sample. The original sample had oil in water concentration of 560± 163 mg/L and the prepared sample had oil in water concentration of 1200± 186 mg/L. To get samples with less oil in water than the original samples field samples with less oil in water concentrations were procured from the waste disposal site.

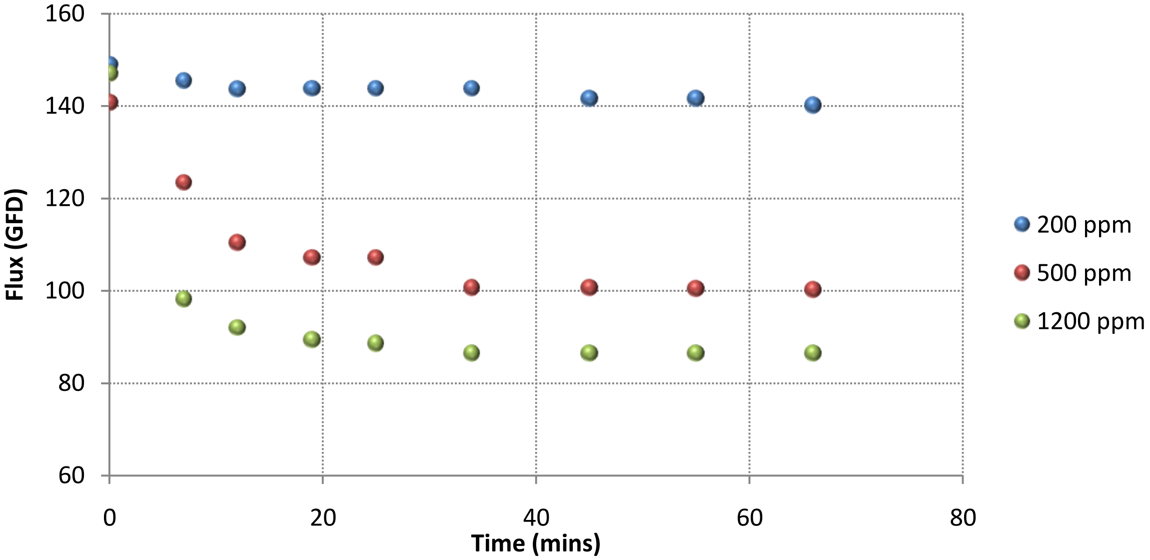


Fig. 3. 12 Oil in water concentration variation in the ceramic filtration of produced water. Oil concentrations are 200± 39 ppm, 560± 163 ppm and 1200± 186 ppm, pH 7.3± 1.5 and salinity 36,000± 5000 TDS mg/L. Ceramic membrane pore size (0.005 micron), transmembrane pressure (15 psi), cross flow velocity (8 ft/s) and temperature (38 C).

In the ceramic filtration of the produced water with and oil in water concentration of 200± 39 ppm, pH 7.3± 1.5 and salinity 36,000± 5000 TDS mg/L with a transmembrane pressure of 15 psi, cross flow velocity of 8 ft/s and temperature of 38 C, the average flux was 143.60 gallons per foot square per day (GFD), maximum permeate flux was 148.94 GFD and the lowest flux was 140.05 GFD, see figure 3.12. Flux decline for the experiment period was less than 6% of the highest recorded flux and there was no significant pressure increase during the experiment. There was 99% rejection of the oil in water concentration by the membranes as the feed concentration and permeate concentration was 182 mg/L and < 1 mg/L respectively. Within the experiment duration most of the feed was treated and the concentration volume factor and the volume reduction were close to 100% i.e. most of the feed was treated, more feed had to be added.

In the ceramic filtration of the produced water with and oil in water concentration of 560± 163 ppm, pH 7.3± 1.5 and salinity 36,000± 5000 TDS mg/L with a transmembrane pressure of 15 psi, cross flow velocity of 8 ft/s and temperature of 38 C, the average flux was

110.06 gallons per foot square per day (GFD), maximum permeate flux was 140.7 GFD and the lowest flux was 100.11 GFD. Flux decline for the experiment period was about 40% of the highest flux and there was no significant pressure increase. There was 99% rejection of the oil in water concentration by the membranes as the feed concentration and permeate concentration was 734 mg/L and < 1mg/L respectively. The volume concentration factor was 4.36 and the volume reduction was 0.23 i.e. the final volume was 23 % of the initial volume. Filtration for this duration and at these condition extracted 77% as effluent.

In the ceramic filtration of the produced water with and oil in water concentration of 1200± 186 ppm, pH 7.3± 1.5 and salinity 36,000± 5000 TDS mg/L with a transmembrane pressure of 15 psi, cross flow velocity of 8 ft/s and temperature of 38 C, the average flux was 95.63 gallons per foot square per day (GFD), maximum permeate flux was 146.96 GFD and the lowest flux was 86.45 GFD. Flux decline for the experiment period was about 42% of the highest flux and there was no significant pressure increase. There was 99% rejection of the oil in water concentration by the membranes as the feed concentration and permeate concentration was 1180 mg/L and 9.4 mg/L respectively. The volume concentration factor was 3.03 and the volume reduction was 0.33 i.e. the final volume was 33% of the initial volume. Filtration for this duration and at these condition extracted 66% as effluent.

Table 3.9 Flux characteristics in the oil in water concentration in the ceramic filtration of produced water

Oil in water Concentration (ppm)	Max Flux (GFD)	Min Flux (GFD)	Average Flux (GFD)	Total Permeate (gal)
200± 39	148.94	140.05	143.60	10.00
560± 163	140.70	100.11	110.06	7.71
1200± 186	146.96	86.45	95.63	6.78

With increasing oil concentration there is a decline in the permeate flux. This correlates to results from the filtration of other oil water wastes [63] from various industries. When the oil in water concentration is lesser than 200 ppm the filtration experiences little or no flux decline compared to higher oil in water concentrations. This is indicative of the role of the oil droplets in the fouling of the membranes. Though the composition of produced water is varied in its physical and chemical properties especially its dissolved components, oil concentration is significant in the fouling of the ceramic membranes. Table 3.9 gives a summary of the fluxes.

At oil in water concentration of 1200 ppm there is a sharp decline in the flux after the initial seven minutes of filtration, by the 15th minute the flux is stabilized and stays that way for most of the experiment duration and this was reproduced almost exactly in repeat runs. The oil particle size also played a role in the flux decline as increased droplet size was an added variable in the contrived sample. Thus the oil concentration and the size of the droplets are important in membrane fouling at high oil concentrations.

3.4 Produced Water Filtration with Hollow Fibre Membranes

3.4.1 Parameter Variation in Produced Water Filtration with Hollow Fibre Membranes

Feed samples for filtration of produced water were procured directly from disposal trucks from the field. Using portable kits concentrations of the oil in water, salinity and some dissolved solids were carried out to see if the feed was within our range. The feed parameter of interest in the filtration of produced water was primarily oil in water concentration and turbidity. The arbitrary produced water was defined to have an oil concentration range of 50 – 300 ppm oil in water, turbidity less than 4000 NTU, pH of 6.5 – 10 and TDS less than 40,000 ppm. Arbitrary operating parameters for hollow fibre filtration was a cross flow velocity of 3.8 ft/s, transmembrane pressure of 10 psi and temperature of 38 C. Temperature was varied between 20 and 52 C, transmembrane pressure varied between 10 and 21 psi and cross flow velocity varied between at 3.81 and 6.69 ft/s. The feed parameter of interests was also varied; oil in water concentration was varied between 200 to 1200 ppm.

The intent of the hollow fibre filtration was particularly to compare the module types i.e. hollow fibre versus the tubular module (ceramic). Unlike the ceramic membranes the hollow fibre membranes are made from polymeric materials, the microza hollow fibre membranes investigated here are made from polyvinylidene fluoride (PVDF). PVDF is hydrophobic i.e. water-repelling and organic and oil attracting, this presented a challenge in the filtration of produced water due to the oil concentration of the feed. At high oil concentration sharp declines in flux was encountered (this is shown in section 3.3.2). Due to the hydrophobic nature of the membrane material the samples used had less oil in the feed than the samples used in the ceramic membrane investigation. The objective of the hollow fibre filtration was to serve as module type comparison. In produced water feed with high turbidity the samples were passed through a 10 micron cartridge filter upstream of the hollow fibre to avoid clogging the membrane.

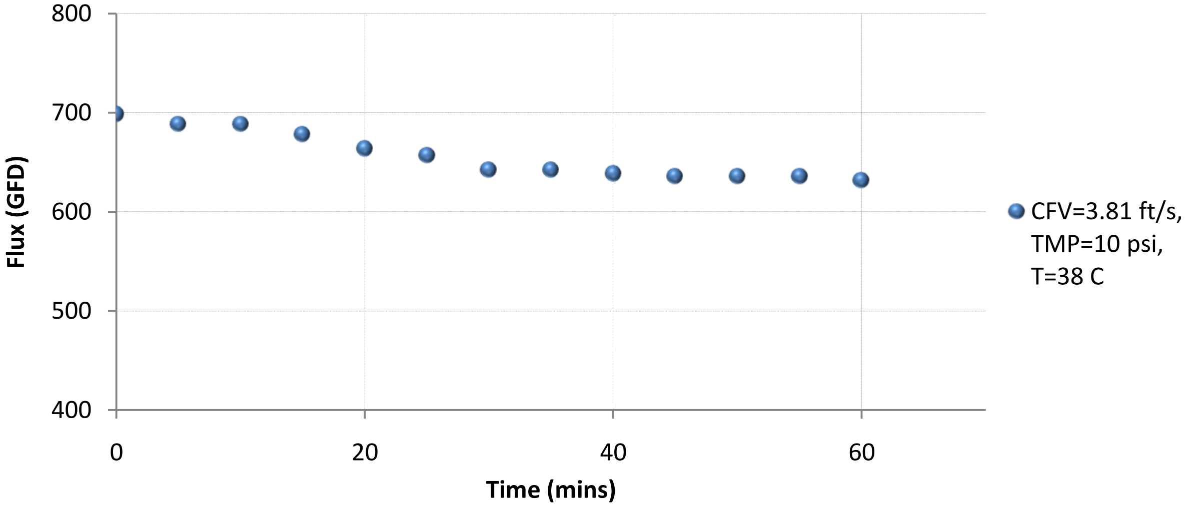


Fig. 3. 13 Hollow fibre filtration of produced water. Oil concentration 155± 100 ppm, pH 7.3± 1.5 and salinity 36,000± 5000 TDS mg/L. Ceramic membrane pore size (0.1 micron), transmembrane pressure (10 psi), cross flow velocity (3.81 ft/s) and temperature (38 C).

In the hollow fibre filtration of produced water with oil concentration 155± 100 ppm, pH 7.3± 1.5 and salinity 36,000± 5000 TDS mg/L filtering at a transmembrane pressure of 10 psi, cross flow velocity of 3.81 ft/s (corresponding to 4 gallons per minute (gpm)) and temperature of 38 C, the average flux was 656.47 gallons per foot square per day (GFD), maximum permeate flux was 698.82 GFD and the lowest flux was 631.76 GFD, see figure 3.13. Flux decline for the experiment period was about 12% of the highest flux decline and there was no significant pressure increase. Solids rejection was 99% in all cases and turbidity reduction was also 99% in all cases and the permeate at all points had turbidity values less than 1 NTU.

There was 99% rejection of the oil in water concentration by the membranes as the feed concentration and permeate concentration was 97 mg/L and < 1 mg/L respectively. The volume concentration factor was 23.5 and the volume reduction was 0.04 i.e. the final volume was 4% of the initial volume. Filtration for this duration and at these condition extracted 95% of the feed as effluent.

Produced water filtration using hollow fiber membranes has a flux that is on average four times the flux of ceramic filtration of produced water with similar feed characteristics. Also, the cross-flow velocity of operation is markedly lower than that of ceramic membrane filtration (3.81 to 8.0 ft/s) and the transmembrane pressures (10 psi to 15 psi). Hollow fibre membranes have large surface area to volume ratio, they operate under low pressure and cross flow velocity and these properties account for the flux superiority of membrane filtration of similar produced water to ceramic membranes. The underlying limitations to hollow fibre membranes is associated with their lower inertness relative to ceramic membranes, their pH ranges are also smaller (though marked improvements have been made), so also is their sensitivity to temperature and chemical solvents are relatively less than ceramics. The PVDF hollow fibre membrane material type was chosen primarily due to its resistance to solvent action allowing better cleaning prospects.

In the filtration of produced water using hollow fibre membranes there is a gradual descent in the flux profile and the flux seems to equilibrate after 40 minutes. This initial decline (10 minute region) could be due to adsorption of the oil droplets on the membrane surface, pore plugging, formation of a gel layer or concentration polarization caused by the oil droplets in the feed. With the hollow fibre the mechanism of fouling is different as there is the possibility of the tube entrance blockage by solids, the fouling on the membrane wall and fouling in the space between individual membrane tubes. These fouling possibilities leave hollow fibre membranes relatively more sensitive to solids concentration and fouling by oil droplets.

Though the fouling mechanism is not ascertained, concentration polarization caused by solids could also be deemed implausible in hollow fibre produced water filtration for the same reasons as in ceramic filtration i.e. the low solids concentration and a higher possibility of oil-membrane interaction. If the mechanism of pore plugging explains the flux decline, then as filtration occurs oil droplets are squeezed into pore spaces constricting the flow of the permeate, the flux equilibrium is achieved at the saturation of the oil concentration. If a gel concentration theory explains the mechanism of flux decline, as filtration occurs oil droplets start to form a layer at the membrane surface and flux equilibrium is achieved when the wall is saturated. Complex fouling possibilities also exist, for example solutes that pass through the membrane pore could accumulate at the passages within the bundles of membranes causing resistance to the flow of permeate. Though the flux rates are impressive long time durability of membrane functioning would require active pre-membrane screens.

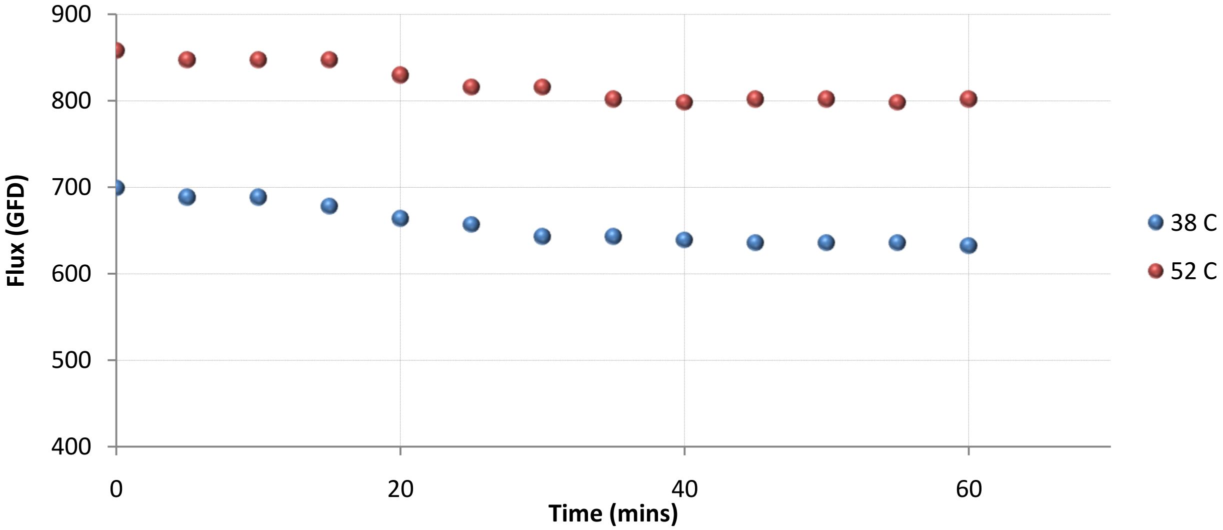


Fig. 3. 14 Temperature variation in the hollow fibre filtration of produced water. Oil concentration 155± 100 ppm, pH 7.3± 1.5 and salinity 36,000± 5000 TDS mg/L. Ceramic membrane pore size (0.1 micron), transmembrane pressure (10 psi), cross flow velocity (3.81 ft/s) and temperature (38 and 52 C).

In the hollow fibre filtration of produced water with oil concentration 155± 100 ppm, pH 7.3± 1.5 and salinity 36,000± 5000 TDS mg/L filtering at a transmembrane pressure of 10 psi, cross flow velocity of 3.81 ft/s (corresponding to 4 gallons per minute (gpm)) and temperature of 52 C, the average flux was 819.92 gallons per foot square per day (GFD), maximum permeate flux was 857.64 GFD and the lowest flux was 801.17 GFD, see figure 3.14. Flux decline for the experiment period was about 7% of the highest flux decline and there was no significant pressure increase. There was 99% rejection of the oil in water concentration by the membranes as the feed concentration and permeate concentration was 168 mg/L and < 1 mg/L respectively Within the experiment duration most of the feed was treated and the concentration volume factor and the volume reduction were close to 100% i.e. most of the feed was treated, more feed had to be added. The fluxes at 38 C are reported above. Table 3.10 gives a summary of the fluxes.

Table 3. 10 Flux characteristics of temperature variation in the hollow fibre filtration of produced water

Temperature	Max Flux (GFD)	Min Flux (GFD)	Average Flux (GFD)	Total Permeate(L)
38 C	698.82	631.76	656.47	38.30
52 C	857.64	801.17	819.92	>40

As temperature increases flux increases. There is an average of 11 GFD flux rise per every degree increase in temperature, this is greater than the flux increase per temperature increase observed in ceramic filtration of produced water. The larger proportional flux increase per temperature rise when compared to ceramic membrane filtration could be due to the greater porosity of the hollow fibre allowing more permeate flow when viscosity reduces or the nature of the membrane material. High temperature does not only give high flux rates the flux decline at this high flux is less than 7% of the highest permeate flux during the duration of the experiment. Barring any temperature limitation on the membrane material higher temperatures would be ideal to run hollow fibre membranes successfully.

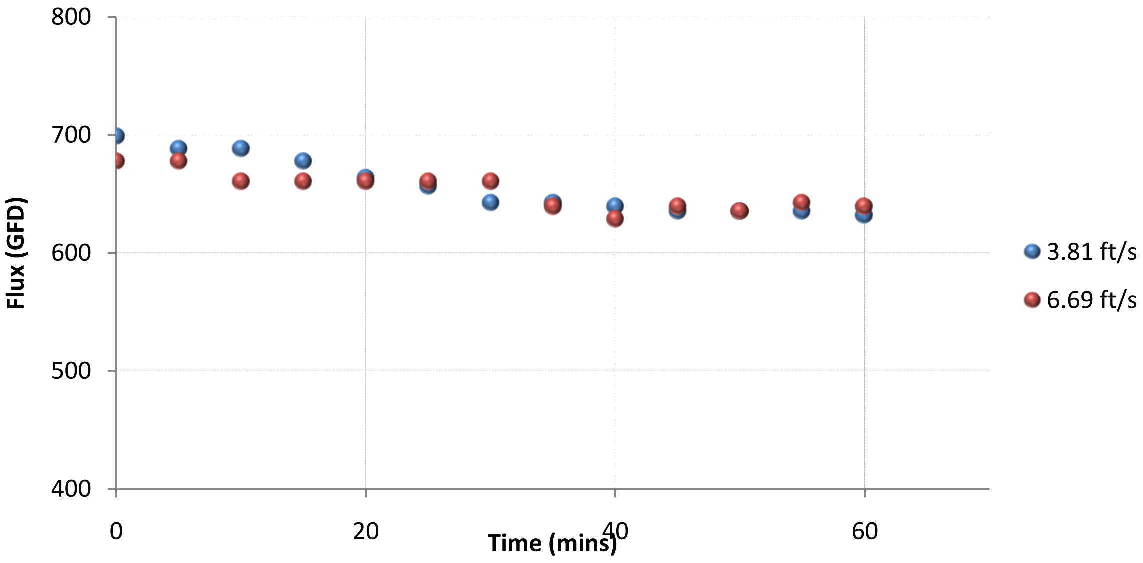


Fig. 3. 15 Cross flow variation in the hollow fibre filtration of produced water. Oil concentration 155± 100 ppm, pH 7.3± 1.5 and salinity 36,000± 5000 TDS mg/L. Ceramic membrane pore size (0.1 micron), transmembrane pressure (10 psi), cross flow velocity (3.81 and 6.69 ft/s) and temperature (38 C).

In the hollow fibre filtration of produced water with oil concentration 155± 100 ppm, pH 7.3± 1.5 and salinity 36,000± 5000 TDS mg/L filtering at a transmembrane pressure of 10 psi, cross flow velocity of 6.69 ft/s (corresponding to 7 gallons per minute (gpm)) and temperature of 38 C, the average flux was 652.16 gallons per foot square per day (GFD), maximum permeate flux was 677.64 GFD and the lowest flux was 638.82 GFD, see figure 3.15. Flux decline for the experiment period was about 9% of the highest flux decline and there was no significant pressure increase. Solids rejection was 99% in all cases and turbidity reduction was also 99% in all cases permeate turbidity was less than 1 NTU. There was 99 % rejection of the oil in water concentration by the membranes as the feed concentration and permeate concentration was 121 mg/L and < 1 mg/L respectively. The volume concentration factor was 20.4 and the volume reduction was 0.04 i.e. the final volume was 4% of the initial volume. Filtration for this duration and at these condition extracted 95% of the feed as effluent.

Table 3.11 Flux characteristics of temperature variation in the filtration of produced water. CFV= cross flow velocity

CFV (ft/s)	Max Flux (GFD)	Min Flux (GFD)	Average Flux (GFD)	Total Permeate(gal)
38 C	698.82	631.76	656.47	38.30
52 C	677.64	631.76	652.16	>40

As the cross flow velocity was increased in the hollow fibre filtration of produced water the flux was similar or reduced. This seems abnormal considering that fact that at increased cross flow velocity more of the material should be forced through the membrane but many hollow fibre membranes operate in the laminar flow region. Hollow fibre membranes have a cross flow velocity range specified by the manufacturers, 6.69 ft/s was the upper limit specified by the manufacturer and at this cross flow velocity there was no advantage. The only difference was the lower permeate decline (<3% difference) between both cross flow velocities. It is thus difficult to deduce the effect on fouling. No middle cross flow velocity was possible considering the equipment specifications. Table 3.11 gives a summary of the fluxes.

The implication of filtration with hollow fibre membranes at their low cross flow velocity and low transmembrane pressures is the low cost of operation as less energy is expended for operation. This could also allow for expenses into raising feed temperature and fouling mitigation technologies to increase the viability of filtering difficult waste streams. Using the tubular hollow fibre membranes as the microza membranes used in our investigation could also mean reduced spacing and thus better optimization of space on portable units. All these advantages are dependent on the compatibility of the hollow fibre with the major feed concentrate in the feed and in this case the oil.

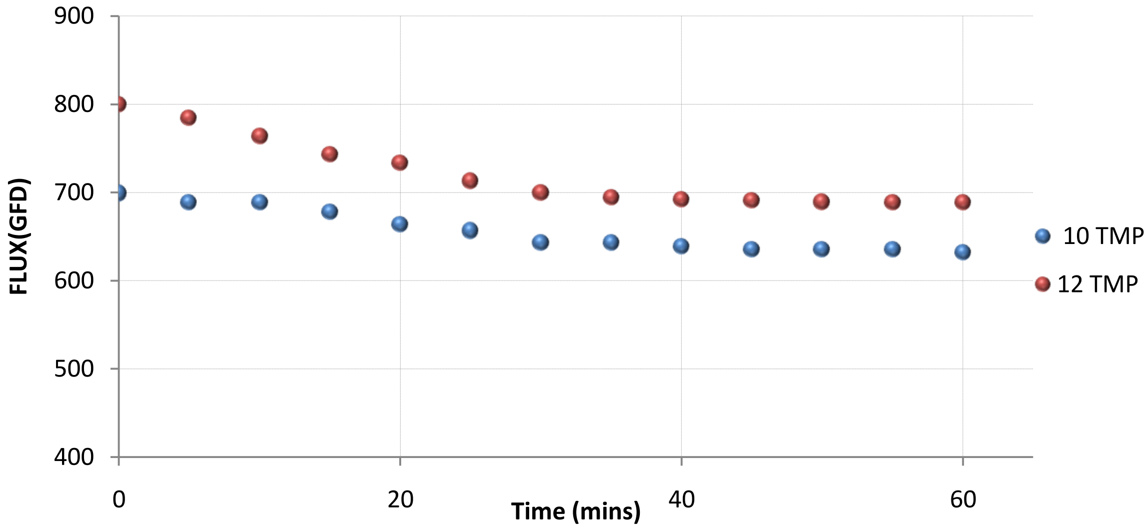


Fig. 3. 16 Transmembrane variation in the hollow fibre filtration of produced water. Oil concentration 155± 100 ppm, pH 7.3± 1.5 and salinity 36,000± 5000 TDS mg/L. Ceramic membrane pore size (0.1 micron), transmembrane pressure (10 and 12 psi), cross flow velocity (3.81 ft/s) and temperature (38 C).

In the hollow fibre filtration of produced water with oil concentration 155± 100 ppm, pH 7.3± 1.5 and salinity 36,000± 5000 TDS mg/L filtering at a transmembrane pressure of 12 psi, cross flow velocity of 3.81 ft/s (corresponding to 4 gallons per minute (gpm)) and temperature of 38 C, the average flux was 721.42 gallons per foot square per day (GFD), maximum permeate flux was 799.45 GFD and the lowest flux was 688.22 GFD, see figure 3.16. Flux decline for the experiment period was about 14% of the highest flux decline and there was no significant pressure increase. Solids rejection was 99% in all cases and turbidity reduction was also 99% in all cases and permeate turbidity was less than 1 NTU.

There was 99% rejection of the oil in water concentration by the membranes as the feed concentration and permeate concentration was 118 mg/L and < 1 mg/L respectively. Within the experiment duration most of the feed was treated and the concentration volume factor and the volume reduction were close to 100% i.e. most of the feed was treated, more feed had to be added. The fluxes at 10 psi are reported above.

Table 3.12 Flux characteristics of temperature variation in the filtration of produced water. CFV= cross flow velocity

TMP (psi)	Max Flux (GFD)	Min Flux (GFD)	Average Flux (GFD)	Total Permeate(gal)
10	698.82	631.76	656.47	38.30
12	799.45	688.22	721.42	>40

Twelve psi transmembrane pressure was the limit allowable for the hollow fibre membrane type used in the investigation. At this transmembrane pressure there was an appreciable increase in the average flux without the attendant flux decline noticed at higher transmembrane pressures using the ceramic membranes. The reasons could be that at 12 psi filtration is still in the pressure controlled region where increases in flux produce an increase in the flux without increasing fouling. Also the pore size is larger than the pore size filtering with ceramics (0.005 vs.0.1), thus the pressure increase at this pore size does not seem to affect flux noticeably. The effect of pressure is still expected to be the same as seen in the filtration using ceramic membranes i.e. there is a pressure where flux decline is rapid; 12 psi transmembrane pressure is below that pressure in the hollow fibre membrane filtration at the specified conditions. Table 3.12 gives a summary of the fluxes.

3.4.2 Oil in Water Variation in the Hollow Fiber Membrane Filtration of Produced Water

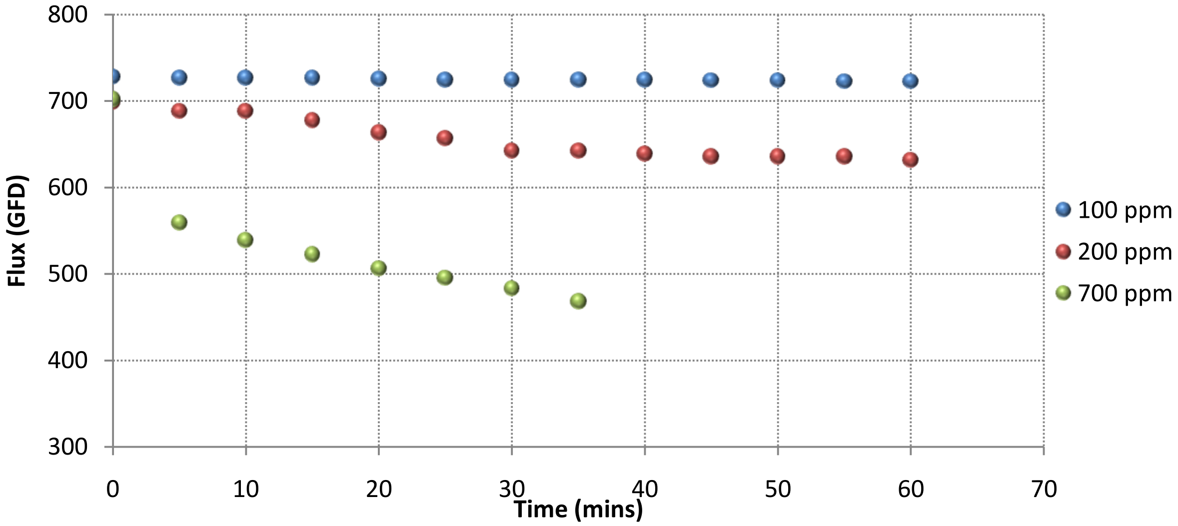


Fig. 3. 17 Oil in water concentration variation in the hollow fibre filtration of produced water. Oil concentrations are 100± 39 ppm, 200± 63 ppm and 716 ppm, pH 7.3± 1.5 and salinity 36,000± 5000 TDS mg/L. Ceramic membrane pore size (0.1 micron), transmembrane pressure (10 psi), cross flow velocity (3.81 ft/s) and temperature (38 C).

In the hollow fibre filtration of the produced water with an oil in water concentration of 100± 39 ppm, pH 7.3± 1.5 and salinity 36,000± 5000 TDS mg/L and transmembrane pressure of 10 psi, cross flow velocity of 3.81 ft/s and temperature of 38 C, the average flux was 724.84 gallons per foot square per day (GFD), maximum permeate flux was 728.23 GFD and the lowest flux was 722.64 GFD, see figure 3.17. Flux decline for the experiment period was less than 2% of the highest recorded flux and there was no significant pressure increase during the experiment. There was 99 % rejection of the oil in water concentration by the membranes as the feed concentration and permeate concentration was 112 mg/L and < 1 mg/L respectively. Within the experiment duration most of the feed was treated and the concentration volume factor and the volume reduction were close to 100% i.e. most of the feed was treated, more feed had to be added.

In the hollow fibre filtration of the produced water with an oil in water concentration of 200± 63 ppm, pH 7.3± 1.5 and salinity 36,000± 5000 TDS mg/L with a transmembrane pressure of 10 psi, cross flow velocity of 3.81 ft/s and temperature of 38 C, the average flux was

656.47 gallons per foot square per day (GFD), maximum permeate flux was 698.82 GFD and the lowest flux was 631.76 GFD. Flux decline for the experiment period was about 10% of the highest flux and there was no significant pressure increase. There was 98 % rejection of the oil in water concentration by the membranes as the feed concentration and permeate concentration was 231 mg/L and 1 mg/L respectively. The volume concentration factor was 23.5 and the volume reduction was 0.04 i.e. the final volume was 4% of the initial volume. Filtration for this duration and at these condition extracted 95% of the feed as effluent.

In the hollow fibre filtration of the produced water with an oil in water concentration of 716 ppm, pH 7.3± 1.5 and salinity 36,000± 5000 TDS mg/L with a transmembrane pressure of 10 psi, cross flow velocity of 3.81 ft/s and temperature of 38 C, the average flux was 534.30 gallons per foot square per day (GFD), maximum permeate flux was 701.76 GFD and the lowest flux was 467.94 GFD. Flux decline for the experiment period was about 88% of the highest flux and there was significant pressure increase. There was 91% rejection of the oil in water concentration by the membranes as the feed concentration and permeate concentration was 716 mg/L and 62 mg/L respectively. The experiment was run for 35 minutes, the volume concentration factor was 1.74 and the volume reduction was 0.57 i.e. the final volume was 57% of the initial volume. Filtration for this duration and at these condition extracted 42% as effluent.

Table 3.13 Flux characteristics in the oil in water concentration in the hollow fibre filtration of produced water

Oil in water Concentration (ppm)	Max Flux (GFD)	Min Flux (GFD)	Average Flux (GFD)	Total Permeate (gal)
100± 39	728.23	722.64	724.84	>40
200± 63	698.82	631.76	656.47	38.30
716	701.76	467.94	534.30	17.08

With increasing oil concentration there is a decline in the permeate flux just as observed using ceramic filters. When the oil in water concentration is lesser than 200 ppm the filtration experiences little or no flux decline compared to higher oil in water concentrations, the flux decline is less than 2% of the highest reported flux. At oil in water concentration of 716 ppm there is a sharp decline in the flux after the initial five minutes of filtration and by the 35th minute the flux was yet to stabilize and the experiment was truncated. Due to fear of destructive fouling the experiment was truncated and not repeated, the values represent a single experiment. The flux decline at 716 ppm was 88% of the highest reported flux value, representing the highest flux decline in all of the experiments; pressure rose by 3 psi over the normal and fear of rising pressure demanded stopping the experiment. Table 3.13 gives a summary of the fluxes.

Though there was a steep flux decline in the ceramic filtration of produced water at high concentrations the flux decline and pressure increase was mild relative to the hollow fibre membrane considering the pores of the ceramic were smaller (0.005 vs. 0.1). The advantages of ceramic membrane over the hollow fibre in this case would be its ability to filtrate much difficult feeds without the limitations imposed by feed components especially organic constituents.

3.5 Summary

The importance of understanding the feed and operational parameter effects in the filtration of a feed cannot be underestimated. Studies of this nature give a baseline snapshot of the dynamics involved in considering if a feed is suitable for filtration. Process engineers and various experts involved in building membrane systems get insight from these types of studies and use them for basic information in planning for pilot studies which are also inevitable. The laboratory system used in the parameter and feed evaluation is the least optimized; it serves strictly for conceptual understanding of the dynamics involved in the feed filtration. With respect to process engineering, mode of operation and operational parameters optimization is significantly low but the proof of concept, understanding of feed behavior, permeate expectation, membrane foot print and information for pilot studies could be gleaned from such results presented in this chapter.

In the filtration of spent drilling fluids using ceramic membranes, we have solids rejection in the upper 90% range; increased solids above 8.8 % solids per volume (~19000 mg/L) significantly reduced the flux. Increased cross flow velocity increased the permeate flux and also helped to delay the inset of fouling, cross flow velocity had the highest impact of all three parameters tested within the range of parameters defined. The effect of increased temperature was also favorable and operation at higher temperature also increased the flux. Increased pressure above 20 psi was detrimental to filtration, flux decline increased at pressures at and above 20 psi. Permeate quality did not change with operating conditions and apart from minimal turbidity differences the permeate quality did not change with pore sizes. Maximum volume concentration achieved was within half of the initial volume. Most importantly the quality of the permeate as regards to solids was low, permeate from the filtration of spent drilling fluids could be used for field related activities such as mud mixing and rig washing apart from the benefits of reduced waste volume.

In the ceramic filtration of produced water, turbidity and solids removal was above 95% in all cases, oil removal in all cases was between 95% -99%. There was an average of about 40% reduction in the flux during normal filtration. Operation at high temperatures had the highest impact on increasing permeate volume and it also helped to prolong the onset of fouling. Cross flow velocity also increased the permeate volume although to a lesser degree than increased temperature. Increased pressure also reduced the flux and accelerated the flux decline. Ceramic membranes could handle a wider range of oil concentration, from 200 ppm to about 1200 ppm oil in water concentration with above 90% percent oil removal in all cases, concentrations above 1200 ppm were not tested. Mechanical removal of solids and turbidity using ceramic membranes in the filtration of produced water was determined to be effective; the turbidity and oil concentrations in the effluent were good enough for desalination processes. Permeate quality did not differ significantly with different pore sizes.

In the hollow fibe filtration of produced water, turbidity and solids removal was above 95% in all cases, oil removal in all cases was between 95% -99%. There was an average of about 20% reduction in the flux during normal filtration. Operation at high temperatures had the highest impact on increasing permeate volume and it also helped to prolong the onset of fouling. Filtration using hollow fibre membranes are at low cross flow velocity and pressure and thus would amount to significant energy saving, increasing cross flow velocity and pressure did not impact the permeate volume significantly. Hollow fibre membranes cannot handle a wider range of oil concentration, oil in water concentrations from 50 ppm to about 700 ppm was used in the experiments and above 90% percent oil removal was achieved in all cases, concentrations above 700 ppm significantly impacted flux negatively. Mechanical removal of solids and turbidity using hollow fibre membranes in the filtration of produced water with less than 200 ppm oil in water concentration was determined to be effective. Permeate volume at comparative operations conditions to ceramic filtration of produced water was four time higher when compared to ceramic membranes and the permeate quality was of equally quality.

CHAPTER IV

MEMBRANE RESISTANCE

4.1 Introduction

During membrane filtration of any feed apart from pure water there is always a reduction in the flux of the membrane with time. For different feeds based on their feed properties and concentration the onset of fouling varies but flux decline occurs after some time. The mechanism of flux decline occurs has been a subject of intense investigation by various authors during membrane filtration [65,68,69]. An added complexity to this investigation is the variation in feed and membrane types under which flux decline is investigated; feed variation is an issue in this investigation especially with produced water. Membrane filtration models that can aptly describe filtration of the feed are beneficial in developing a sustainable membrane filtration system. Understanding the effect operational and feed parameters have on flux decline would also give a robust assessment of the filtration mechanism. Also, the understanding of fouling mechanism(s) would be useful in the determination of effective cleaning methods to maintain membrane integrity.

Two major components are believed to contribute to permeate flow resistance during microfiltration; the first is associated with the membrane, its properties and the propensity for pore blocking. The second is associated with the membrane boundary layer, the generation and or absence of a fouling layer at the interface of the membrane [64]. The decline of permeate flux is due to the combined effect of these two factors, the real challenge has been the identification of the contributing role or proportion of each individual factor and factors within them. A direct approach to getting a clearer picture is arrived at through investigation of the flux decline curves; an analysis of this curves and their application to existing models or using them to develop totally new models help in the understanding of contributing factors to permeate flux decline.

In this chapter, two different models aimed at describing filtration are considered. The first model, developed by Hermia [68], called the constant pressure blocking filtration laws are presented in their modified linearized forms relating the permeate flow rate, permeate volume and time with the filtration constants for each model. The second model, the resistance in series model, aimed at describing resistances during filtration quantifies the various resistances affecting filtration showing their influence on the total resistance. The results in the resistance in series model are further reported as a ratio of the resistance to the intrinsic membrane resistance to give a better estimate of the resistance magnitude.

4.2. Constant Pressure Filtration Models

Hermia's[68] filtration laws were applied in this section to determine if they could be used to describe the mechanism of filtration during membrane filtration of produced water and spent drilling fluids using ceramic membranes and hollow fibre membranes. Flux decline curves from filtration experiments carried out were matched to the four filtration mechanisms described by Hermia to determine which adequately described the observed flux decline. Hermia attributed flux decline to four mechanisms under constant pressure filtration; complete blocking, intermediate blocking, standard blocking and cake filtration. These blocking models are variants describing possible methods of pore blocking or cake layer formation during membrane filtration.

In the complete blocking model, the underlying assumption is that each particle in the feed reaching the membrane pore actively seals the pores and particles are not superimposed upon each other, in this respect the blocked surface area is deemed proportional to the permeate volume. The rate of change in the amount of open pores is directly proportional to the rate at which particles are transported to the membrane surface. This model also assumes that the formation of a cake or layer at the membrane surface is negligible. Particles in the model as it relates to our feed for water based wastes could be solid particles in the drilling mud or oil droplets in the produced water.

The second model, the intermediate blocking model, is a variation of the complete blocking model. In this model the assumption is also that amount of blocked pores on the membrane is proportional to the permeate volume; it differs from the complete blocking model in that it does not assume that there is no superimposition of the particles. In this less limiting version of the complete blocking model, the assumption is that each particle would not block the pores of the membrane and that there is superimposition of the particles on one another. Here the rate of transport of particles to the membrane is not directly proportional to the volume of permeate. It is assumed in this model that second particle layer has an equal chance of settling on the first layer or the membrane surface and that the suspension is homogenous.

The third model, the standard blocking model concerns itself with the size of the feed particles. In this model it is assumed that most of the feed particle sizes are less that the pore diameter allowing the deposition of the particles in the pores and reducing the available pore volume. In the standard blocking model the pore volume decreases proportionally to the amount of particles in the feed that are deposited in the pore spaces. Other assumptions inherent in this model are that the membrane pores are largely uniform in their diameter and length and that each particle has the same chance of deposition into the pore spaces. This model is used to explain the case for filtration of feed with smaller particles.

The fourth model the cake filtration model concerns itself also with the size of the feed particles. This model is used to explain the case of large particles that cannot enter most of the membrane pores [64]. In the cake filtration model the assumption is that majority of the particles are bigger than the membrane pores and cannot enter the pores but are deposited on the membrane surface forming a filter cake. In this model permeate volume is proportional to the increase in filter cake thickness i.e. as the filter cake thickness increases the permeate volume reduces. Assumptions inherent in this model are that the membrane pores are largely uniform in their diameter and length and that each particle has the same chance of deposition into the pore spaces.

Mohammadi [65] provides the characteristic forms of the equations of these four models as this equations can be expressed in simple linear equations (Table 4.1) relating the permeate flow rate (Q), permeate volume (V) and time (t) with the filtration constants for each model (K_b, K_i, K_s and K_c) and initial permeate flow Q_o. In other to obtain the filtration constants (K_b, K_i, K_s and K_c), the experimental data (Q, V and Qo) were plotted for each form of equation in Table 4.1. According to Mohammadi [65], the initial slope of the curve obtained at the value of V or t equals to zero allowing the calculation of each filtration constant and the intercept is the initial flow Qo. The constants K_b, and K_i are directly related to blocked surface area per unit permeate volume, K_s is dependent on the volume of particles retained per unit permeate volume and K_c depends on both cake resistance and concentration. Q is the permeate flow rate,Q_0 the initial permeate flow, t the time and K_b, K_i, K_s and K_c the filtration constants.

Table 4.1 Constant pressure filtration models

Model	Equation
Complete blocking filtration Model	$Q = Q_0 - K_bV$
Intermediate blocking filtration model	$1/_Q = K_it + 1/_{Q_0}$
Standard blocking filtration model	$\sqrt{Q} = \sqrt{Q_0} - (K_s\sqrt{Q_0}\ V/_2)$
Cake filtration model	$1/_Q = 1/_{Q_0} + K_cV$

4.2.1 Ceramic Filtration of Spent Drilling Fluid

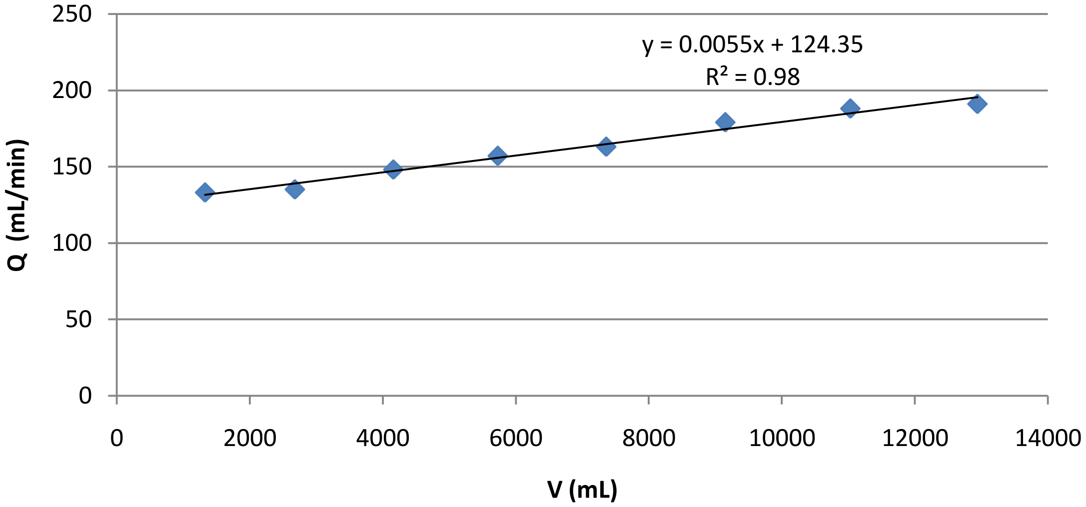


Fig. 4. 1 Plot of Q against V in complete blocking filtration model in the ceramic filtration of spent drilling fluids.

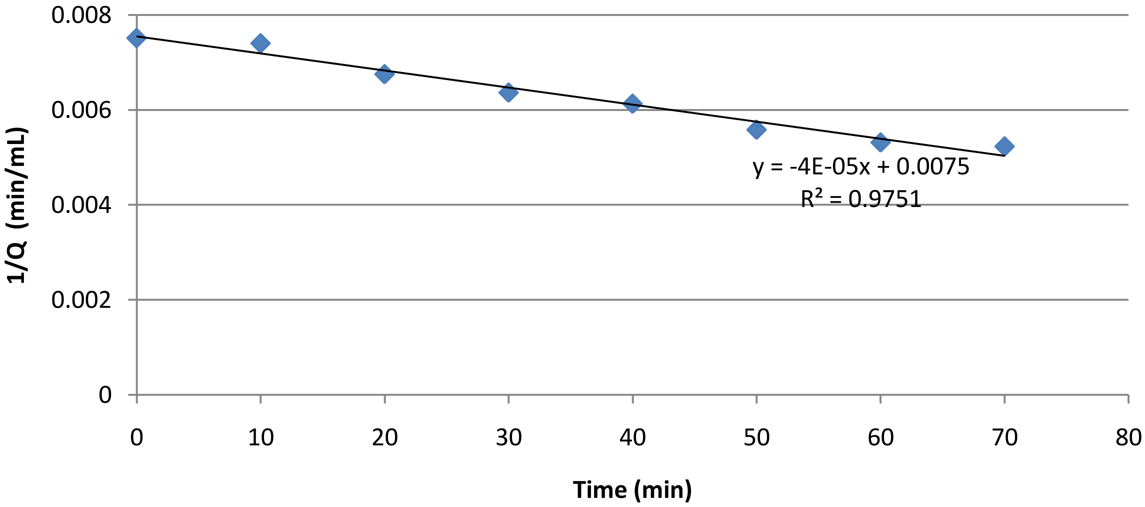


Fig. 4. 2 Plot of 1/Q against t in intermediate blocking filtration model in the ceramic filtration of spent drilling fluids.

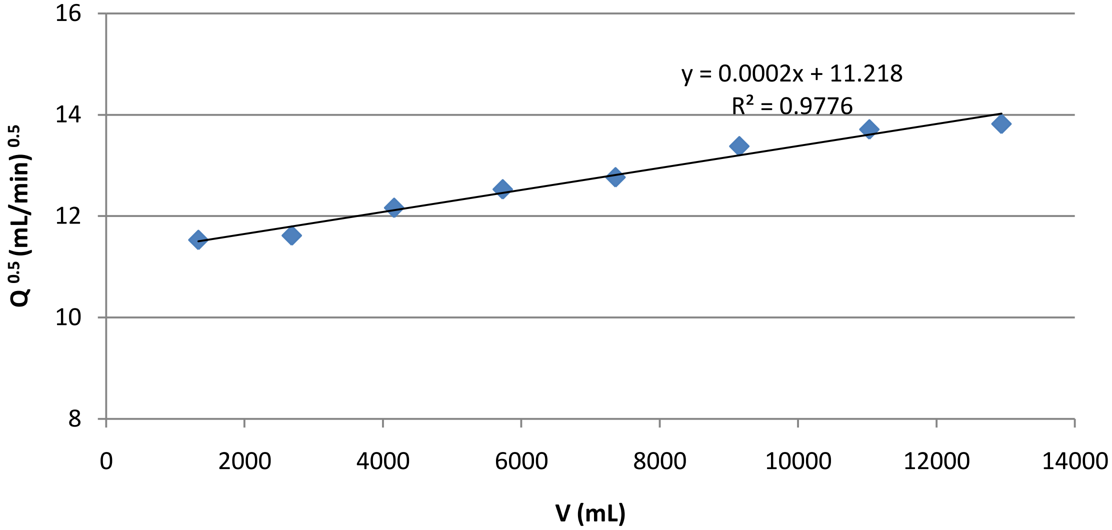


Fig. 4. 3 Plot of $Q^{0.5}$ against V in standard blocking filtration model in the ceramic filtration of spent drilling fluids.

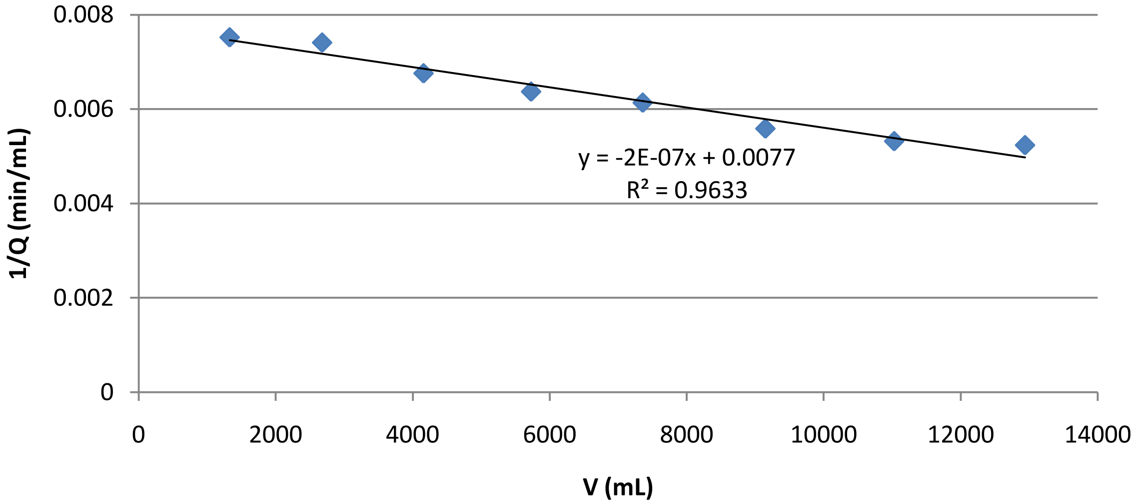


Fig. 4. 4 Plot of 1/Q against V in cake filtration model in the ceramic filtration of spent drilling fluids.

Due to the hump in flux values observed in the filtration of spent drilling fluids (chapter III) the graphs produced were discontinuous except for data at high cross flow velocity and high temperature. The graphs presented here were from using data from the experimental results of filtration of spent drilling fluids at cross flow velocity of 16 ft/s, transmembrane pressure of 15 psi and temperature of 38 C.

The results of fitting the data from the ceramic membrane filtration of spent drilling fluids to the filtration models by plotting the rate of permeate volume (Q or 1/Q or $Q^{0.5}$) with either filtration volume (V) or the filtration time (t) is presented in figures 4.1 -4.4. From the results we see that all models show a high correlation in explaining the filtration mechanism with complete blocking filtration showing a slightly stronger correlation and cake filtration showing the least. From this it seems that using the Hermia models no model adequately explains the filtration in the spent drilling fluids filtration or no model is dominant though the co-existence of different model behavior at different stages during filtration has been reported [48].

The spent drilling fluid samples had a high solids concentration (> 8% solids per volume ~ 19,000mg/L) with a wide particle size range. Most models describing filtration with solids use hard spherical particles that remain a definite size through the model build-up, the nature of the particle in spent drilling mud are markedly different. The particles in the spent drilling mud are earth and they are constantly breaking up into smaller particles due to shear, the distribution is also wide with particles sizes ranging from sand to colloidal barite particles. The data used were generated under high cross flow velocity, thus a high mass flow of the samples is passing through the membrane and the existence of the various models at different periods in filtration is possible though no single model adequately explains the filtration phenomenon.

4.2.2 Produced Water Filtration with Ceramic Membranes

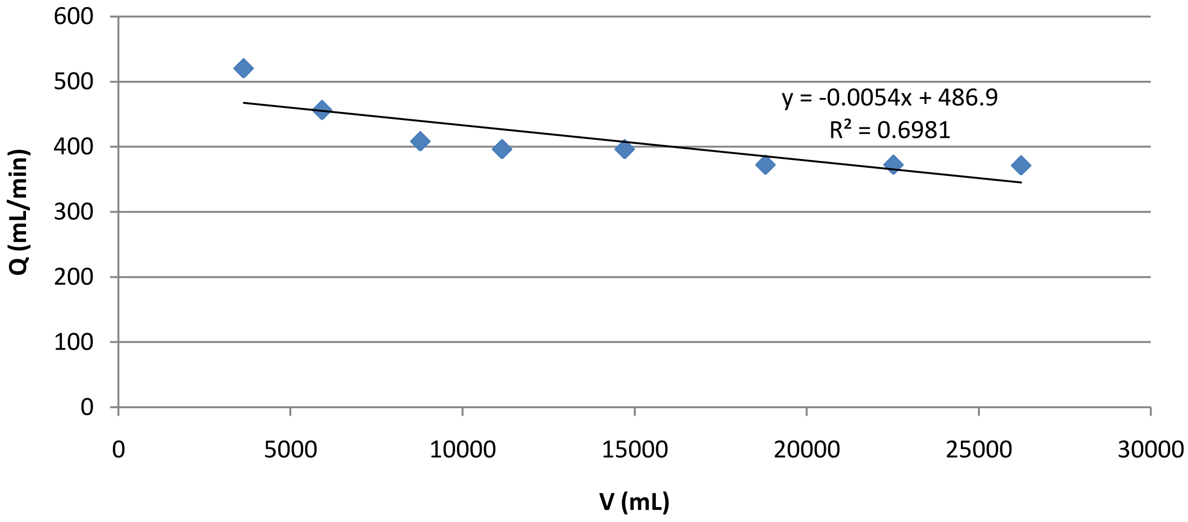


Fig. 4. 5 Plot of Q against V in complete blocking filtration model in the ceramic filtration of produced water.

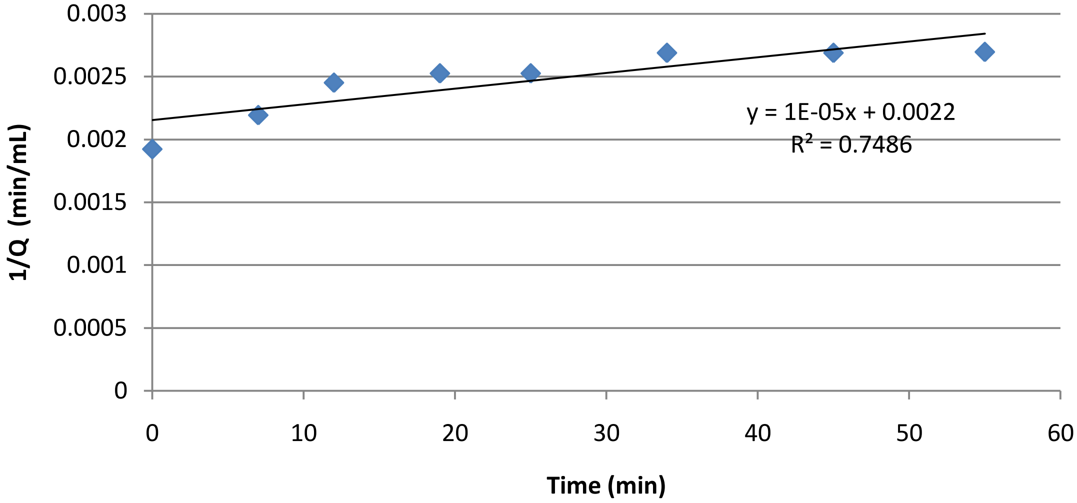


Fig. 4. 6 Plot of 1/Q against t in intermediate blocking filtration model in the ceramic filtration of produced water.

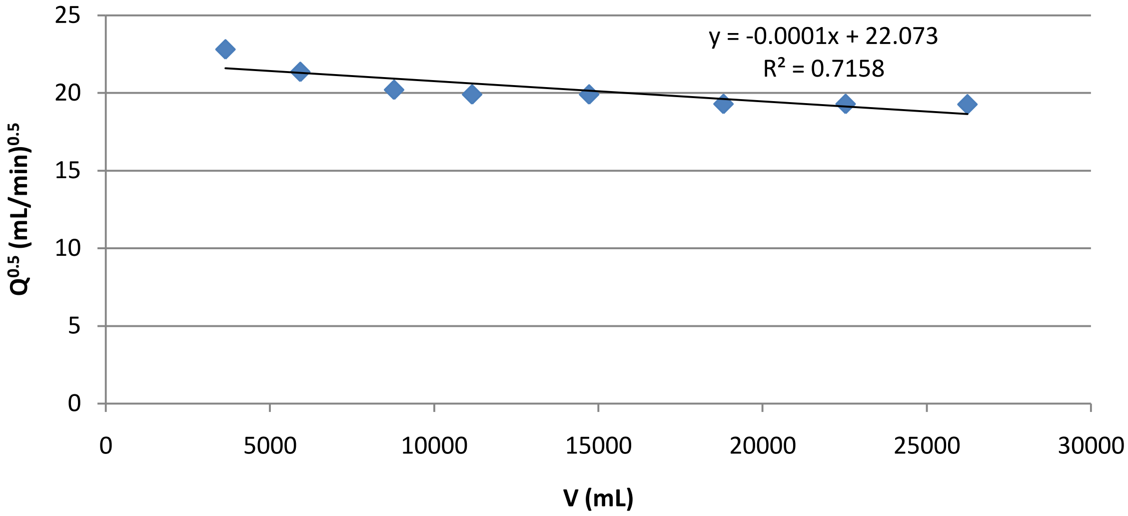


Fig. 4. 7 Plot of $Q^{0.5}$ against V in standard blocking filtration model in the ceramic filtration of produced water.

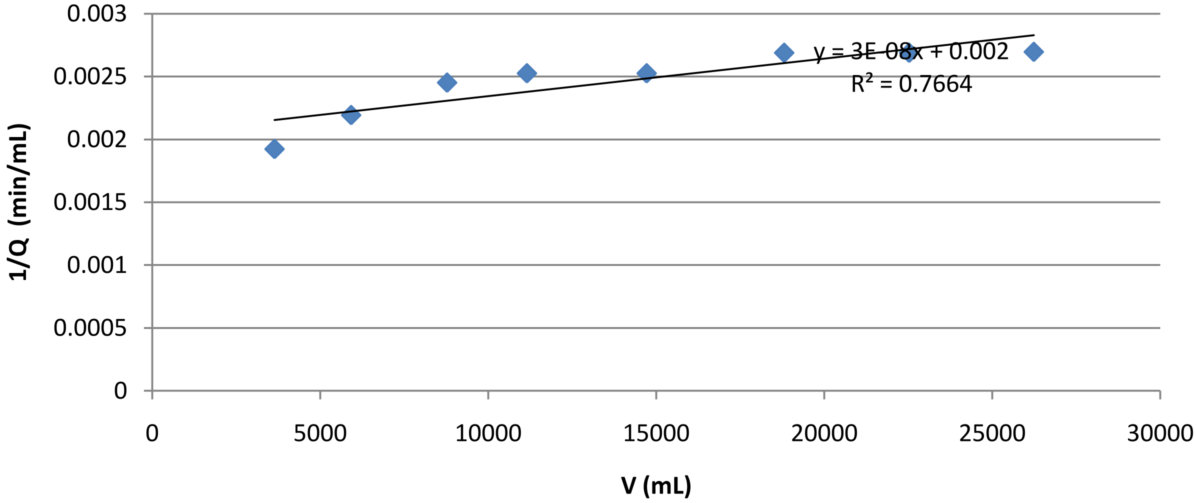


Fig. 4. 8 Plot of 1/Q against V in cake filtration model in the ceramic filtration of produced water.

The results of fitting the data from the ceramic membrane filtration of produced water to the filtration models by plotting the rate of permeate volume (Q or 1/Q or $Q^{0.5}$) with either filtration volume (V) or the filtration time (t) is presented in figures 4.5 -4.8. From the results we see that all models show poor correlation in explaining the filtration mechanism in the filtration of produced water with ceramic membranes. This re-enforces the notion that a complex interaction exists between the oil droplets, membrane surface and membrane pores that is not easily described with the simplified models, using the modifications by Kotuniewicz et al [69] to the Hermia model did not fit either (results not shown). Various authors have described various filtration mechanisms in the filtration of produced water using different membrane and under different conditions. Hu [48] describes different filtration models operating at different periods during produced water filtration, showing the first stage expressing some blocking filtration and the second stage cake filtration while others describe a dominance of a filtration mechanism but usually with simulated oil contaminated water [66,67].

4.2.3 Produced Water Filtration with Hollow Fibre Membranes

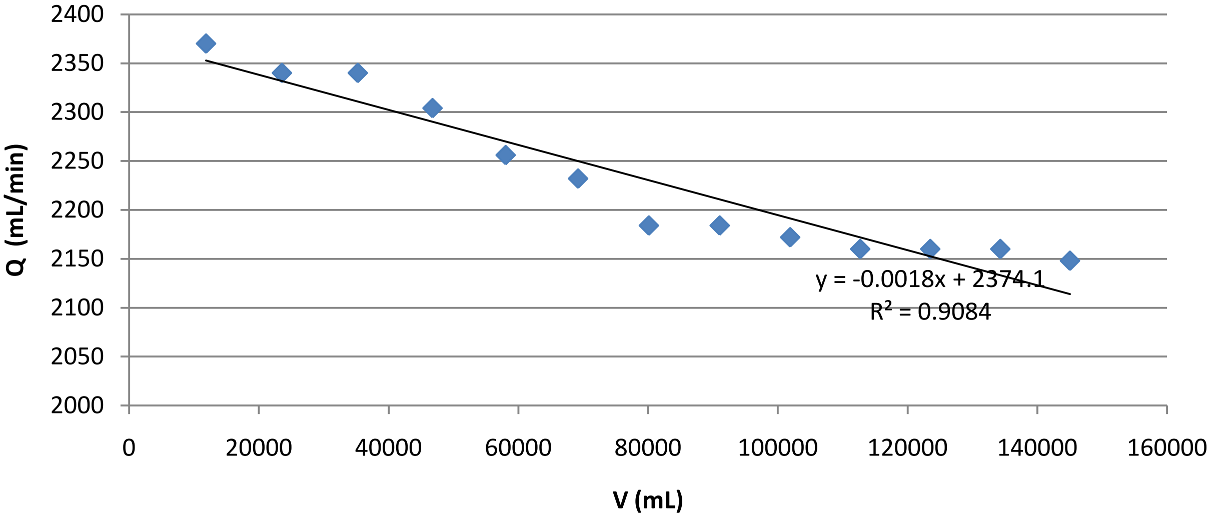


Fig. 4. 9 Plot of Q against V in complete blocking filtration model in the hollow fibre filtration of produced water.

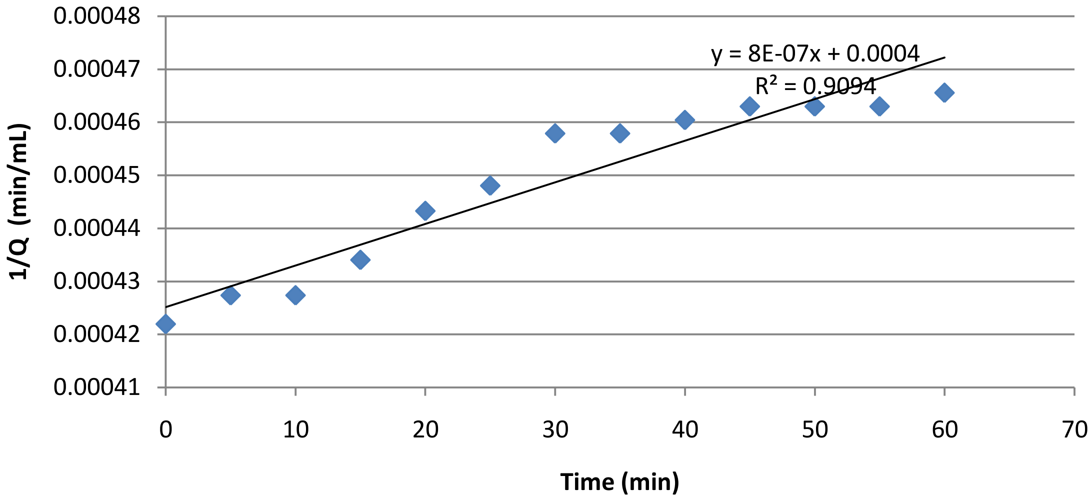


Fig. 4. 10 Plot of 1/Q against t in intermediate blocking filtration model in the hollow fibre filtration of produced water.

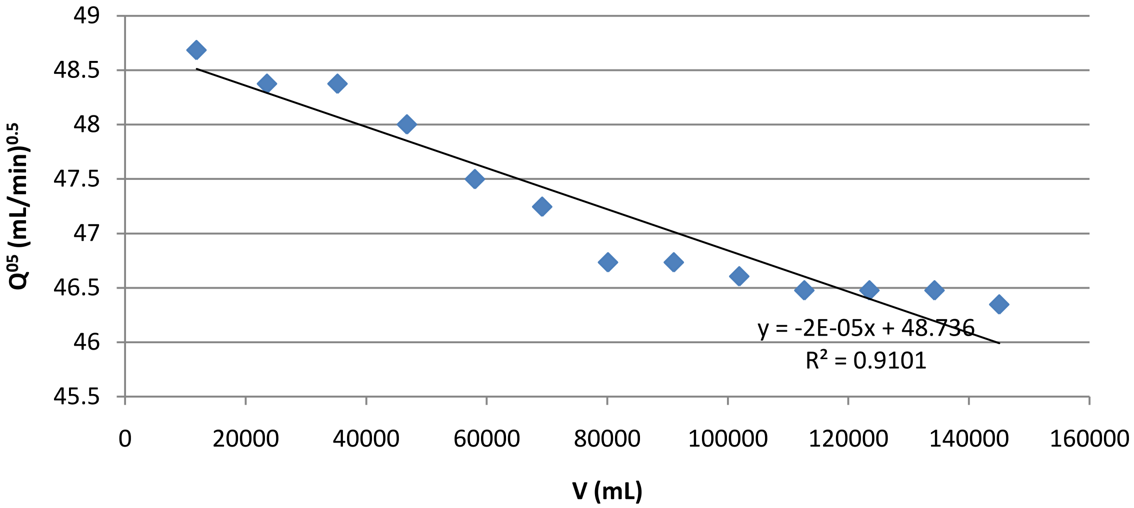


Fig. 4. 11 Plot of $Q^{0.5}$ against V in standard blocking filtration model in the hollow fibre filtration of produced water.

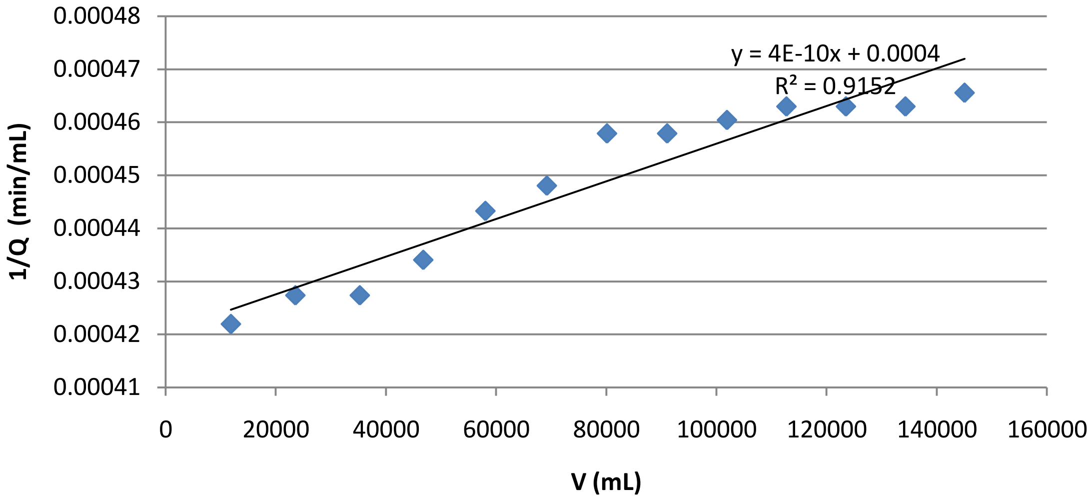


Fig. 4. 12 Plot of 1/Q against V in cake filtration model in the hollow fibre filtration of produced water.

The results of fitting the data from the hollow fibre membrane filtration of produced water to the filtration models by plotting the rate of permeate volume (Q or 1/Q or $Q^{0.5}$) with either filtration volume (V) or the filtration time (t) is presented in figures 4.8 -4.12. From the results we see that all models show a medium correlation in explaining the filtration mechanism with cake filtration showing a slightly stronger correlation and complete blocking showing the least, a reversal of ceramic filtration of spent drilling fluids. From this it seems that using the Hermia models no model adequately explains the filtration in the hollow fibre filtration of produced water, there were no appropriate models found in literature that could suitably be applied to the hollow fibre membrane used.

4.3 Resistance Determination

Due to complexities in describing accurately the filtration mechanism, another beneficial approach would be to use pressure and flux differences to determine the resistances involved in membrane filtration. Another model designed to increase the understanding of membrane fouling is the membrane resistance model and it is one of the most applicable fouling models [64]. This model better describes the entire pressure-flux behavior during ultrafiltration or microfiltration i.e. pressure-controlled at low pressures, pressure-independent at high pressure [40]. The resistance in series model is based on the assumption that there are several distinct resistances in series which affect the transmembrane flux and are indicative of fouling. Central to the resistance model is an understanding of the relative proportion of the various membrane resistances under different filtration conditions, this is crucial to understanding fouling/flux decline. Since the blocking models proposed by Hermia [68] were inadequate to explain flux decline in the filtration of water based drilling wastes the resistance in series model is used here to analyze membrane resistances.

During filtration there are different resistances; there is the resistance solely due to the membrane itself, resistance due to adsorption, resistance due to concentration polarization and resistance due to irreversible and reversible fouling [64]. These resistances are active or passive in the fouling of membranes and are affected to a large degree by the concentration of feed constituent's and operational parameters. Darcy's law is used to determine filtration resistance in permeate transport through porous membranes:

$$J = \frac{P_T}{\mu\, R_t} \tag{4.1}$$

Where J is the permeate flux, P_T is the transmembrane pressure, μ is the viscosity of the permeate and R_t is the total membrane resistance. Different models subdivide the components of total membrane resistance R_t, differently; the definition according to Choi et al [64] is adopted. According to Choi et al

$$R_t = R_m + R_{ad} + R_{cp} + R_f \tag{4.2}$$

Where R_m is the membrane resistance, R_{ad} the resistance due to adsorption, R_{cp} resistance due to concentration polarization and R_f resistance due to fouling. Therefore equation 4.1 can be re-written as

$$J = \frac{P_T}{\mu(R_m + R_{ad} + R_{cp} + R_f)}$$

(4.3)

These resistances are described as follows:

Membrane resistance R_m

During filtration of an ideal feed such as reverse osmosis water which is devoid of solutes the only resistance encountered is the membrane resistance R_m. R_m is the hydraulic resistance of the membrane i.e. the intrinsic membrane resistance determined by using pure water as the feed. R_m is useful for modeling purposes, evaluating the effectiveness of cleaning procedures and for charting the long time stability of the membrane [49]. At a fixed operating pressure, the membrane resistance is a function of the viscosity of the feed water. R_m and the pure water flux J_w are related by

$$J_w = \frac{P_T}{R_m}$$

(4.4)

Where J_w is pure water flux, P_T is the transmembrane pressure and R_m is the membrane resistance.

Resistance due to adsorption R_{ad}

When the membrane is in contact with the feed solution solute molecules interact with the membrane surface and adsorb to the membrane. This physico-chemical interaction between the membrane and the solutes could result in resistances to the flow of permeate and it is independent of the presence of permeate flux. Filtration resistance due to adsorption is thermodynamically unavoidable but its contribution to the total filtration resistance is very small [64,70,71]in most cases. In exceptionally cases such as feed with high solute concentration for example ultra saturated brines wastes could make the contribution due to adsorption significant.

Resistance due to concentration polarization R_{cp}

Resistance due to concentration polarization is always confused with resistance due to true fouling, they are different and for the purpose of the different resistances in this model it shall be strictly defined in operational terms. Concentration polarization is fouling where the membrane flux can be recovered by "rinsing" the membrane with de-ionized or reverse osmosis water at the same operational conditions at which filtration of the feed occurs. The concentration polarization layer is believed to be caused by loose accumulation of particles at the membrane surface layer existing at the threshold of hydraulic resistance to permeate flow.

Resistance due to fouling R_f

Resistance due to fouling is the most important of all the resistances as it can be reduced by proper techniques in practical applications [64] or can cause significant losses in filtration operations. According to the classification by Choi et al., the resistance due to fouling is subdivided based on the strength of attachment of the foulants onto the membrane surface. Based on this classification resistance due to fouling is subdivided into reversible and irreversible fouling

$$R_f = R_{rf} + R_{if} \tag{4.5}$$

Where R_f is resistance due to fouling, R_{rf} is reversible fouling and R_{if} is irreversible fouling.

Reversible fouling is fouling caused due to loosely attached foulants and the flux can be reclaimed by "flushing" the membrane at high shear for a specified amount of time with reverse osmosis or distilled water. Cleaning with respect to R_{if} and R_{cp} differ in the magnitude of shear needed to dislodge the foulants predicated on the degree of attachment of the foulants to the membrane surface. Rinsing involves replacing the stream feed with distilled water or reverse osmosis water to filter through the membrane at the same operational conditions during feed filtration. Flushing does not only require using reverse osmosis or de-ionized water to clean the membrane but the filtration at higher cross flow velocity than the operating condition. It involves filtration at low pressure and high cross flow velocity creating a high shear low pressure condition to remove the attached foulants.

Irreversible fouling is fouling where the flux cannot be regained after flushing and or rinsing and would require some form of treatment to regain the flux. In irreversible fouling operational parameter variations to create conditions where reverse osmosis water or de-ionized water is used to recover flux is largely ineffective. Irreversible fouling can only be treated through chemical means or some special membrane treatment that addresses the root cause of the fouling either physical or chemical. The term irreversible does not connote an irrevocable loss of the membrane filtering capability but rather a loss that requires some form of cleaning aside from operational parameter variation.

The classification of the fouling resistances in better viewed as special cases of concentration polarization where the degree of attachment of the foulants varies progressively. Concentration of particles onto the membrane surface reaches its maximum value after a short period due to high initial flux and then the gel and cake layers start to form. It is assumed that the three layers, the concentration polarization layer, reversible fouling layer and the irreversible fouling layer simultaneously exist on the membrane surface. As filtration progresses, the inner fouling layer near the membrane surface becomes more compacted resulting in a higher density. By the same mechanism the initial reversible fouling layer becomes more dense and attached to the surface of the membrane surface which means higher resistance to shear force and in the same vein the reversible fouling layer is transformed into irreversible fouling layer [64].

The experimental study to determine the various filtration resistances and their corresponding resistance measurements for the resistance in series model was carried out in three phases adopted from Choi et al [64] with slight modifications as shown in Figure 4.13.

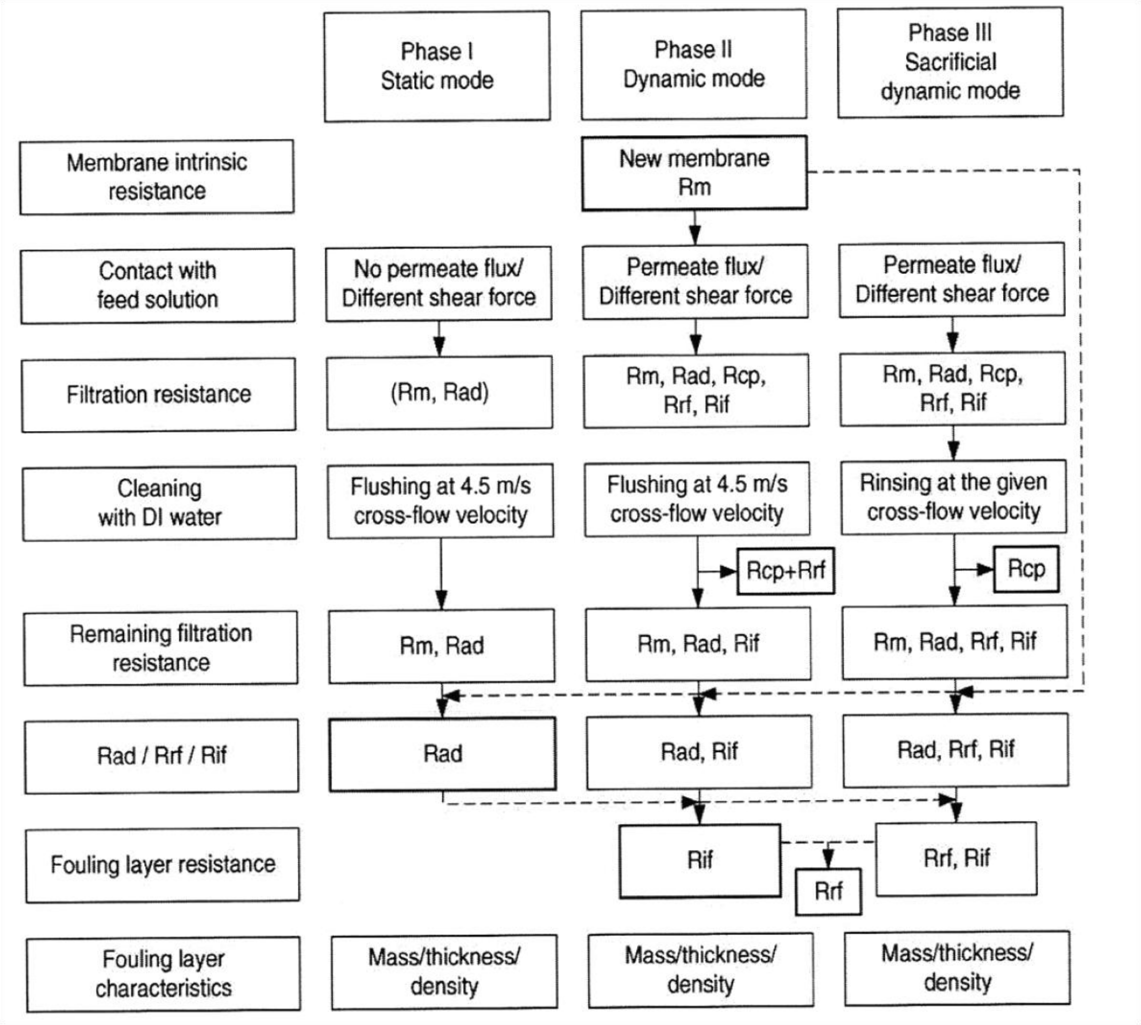


Fig. 4. 13 Test sequence for evaluating the various filtration resistances and their corresponding fouling layers (adopted from [64]).

Phase I

The first phase, called the static mode, is the mode where there is no permeate flux and the transmembrane pressure is 0 psia. In the static mode the feed is contacted with membrane for 4 hours for spent drilling fluids and 6 hours for produced water in the membrane housing, the feed is pumped to fill the membrane housing. After these hours the membrane is then flushed with RO water at high cross flow velocity and low pressure. In this static mode the total resistance of the fouled membrane consists of R_{ad} and R_m, the adsorption and membrane resistances. Therefore

$$R_{ad} = R_t - R_m \tag{4.6}$$

Where R_t is the filtration resistance of fouled membrane in the static mode.

Phase II

Phase II is the dynamic mode, filtration of the feed occurs at the filtration transmembrane pressure of and cross flow velocity for 4 hours uninterrupted for drilling fluids and six hours for produced water. After filtration for four hours the membrane is then flushed for 5 minutes. Flushing in this experimental setup involves cleaning the membrane at high cross flow velocity and low transmembrane pressure for 5 minutes. The total difference in total filtration resistance of the fouled membrane before and after flushing was defined as the sum of R_{cp} and R_{rf}

$$R_{cp} + R_{rf} = R_{t,240} - R_{t,f} \tag{4.7}$$

Where $R_{t,240}$ is the filtration resistance after feed filtration for four hours and $R_{t,f}$ is the filtration resistance after flushing following the four hour filtration, mass and thickness of the fouled membrane after flushing resulted from R_{ad} and R_{if}.

Phase III

Phase III called the sacrificial dynamic mode helps in determining the resistance due to concentration polarization. The same procedure was carried out again as in Phase II but this time after four hours of filtration where the difference in final permeate fluxes between Phase II and Phase III was less than 5%, rinsing instead of flushing was applied. Rinsing involves filtration with RO water at the same filtration condition at which the feed was filtered. Since rinsing removes concentration polarization, R_{cp} is

$$R_{cp} = R_{t,240} - R_{t,r} \tag{4.8}$$

Where $R_{t,r}$ is the filtration resistance after rinsing. Mass and thickness of the fouled membrane after rinsing resulted from R_{ad}, R_{rf} and R_{if}. R_{rf} was determined by subtracting equation (4.8) from (4.7). Finally the filtration resistance by irreversible fouling was determined as

$$R_{if} = R_{t,f} - R_m - R_{ad} \tag{4.9}$$

This same procedure was carried out for the ceramic filtration of produced water and spent drilling fluids. This procedure was carried out at the different operational parameters of pressure and cross flow velocities and under the various feed constituents i.e. oil and solids concentration variation.

4.3.1 Resistance in Series Model for Ceramic Membrane Filtration of Spent Drilling Fluid

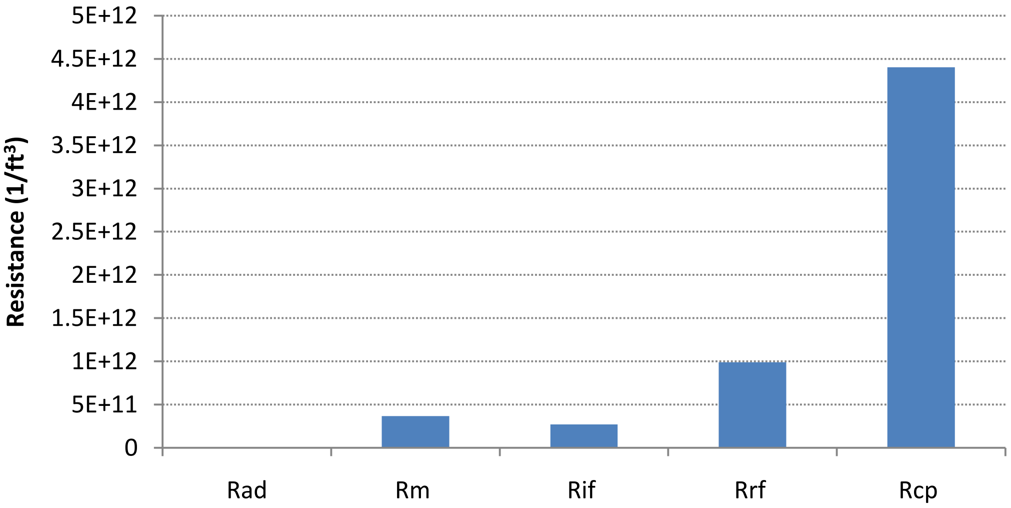


Fig. 4. 14 Different resistances in the ceramic filtration of spent drilling. Solids concentration (8.8± 0.5% vol) and pH (9.5). Ceramic membrane pore size (0.2 micron), transmembrane pressure (15 psi), cross flow velocity (10.08 ft/s) and temperature (38 C).

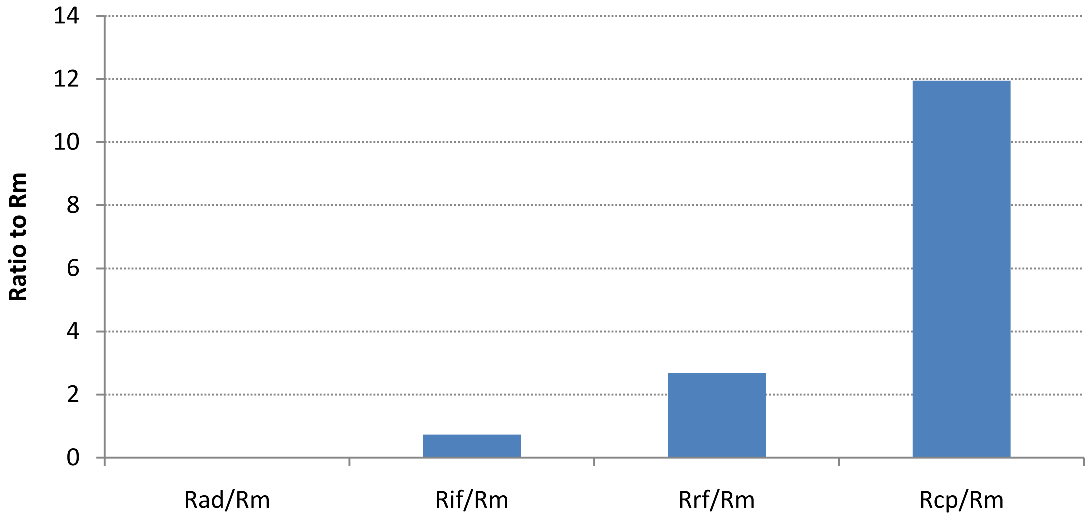


Fig. 4. 15 Ratio of the various resistances to membrane intrinsic resistance in the ceramic filtration of spent drilling. Solids concentration (8.8± 0.5% vol) and pH (9.5). Ceramic membrane pore size (0.2 micron), transmembrane pressure (15 psi), cross flow velocity (10.08 ft/s) and temperature (38 C).

The resistances involved in the ceramic filtration of spent drilling fluids under the chosen arbitrary condition are shown in figure 4.14. At this condition resistance due to concentration polarization R_{cp} is the dominant resistance while other resistances are significantly lesser, resistance due to reversible fouling R_{rf} is the second most significant resistance under this condition. For the fouling studies a brand new ceramic membrane was used in all the experiments. It was noticed that using a new membrane the intrinsic membrane resistance could obscure the contribution of other resistances and the same effect was noticed with fouled membranes (used over two years) as the intrinsic membrane resistance obscured the proportion. Reporting the different resistances as a ratio of the intrinsic membrane resistance gave a more robust assessment of the role of the different resistances and gave an accurate assessment of the contributing membrane resistances.

This ratio comparison allows for the unique development of a practical tool to monitor membrane fouling and integrity by simple tests during membrane filtration and clean-up as would be shown. It also eliminates false fouling representation under various conditions and allows for evaluation of membrane integrity at any point during active membrane use especially when the initial pure water flux is not 100% obtainable. Figure 4.15 reports the various resistances as a ratio of the intrinsic membrane resistance and the advantage of reporting in this manner is not apparent but would be apparent other circumstances. From figures 4.14 and 4.15 it is seen that resistance due to adsorption is non-existent in contributing to fouling in the filtration of spent drilling fluids and this supports the findings of [64,70,71] in the filtration of other feeds. Table 4.2 shows the various resistances at different pressures.

Table 4.2 Various resistances in the ceramic filtration of spent drilling fluids at different pressures. Solids concentration (8.8±0.5% vol), pH (9.5). Ceramic membrane pore size (0.2 micron), transmembrane pressures (7, 15 and 20 psi), cross flow velocity (10 ft/s) and temperature (38 C)

Pressure (psi)	R_m ($1/ft^3$)	R_{if} ($1/ft^3$)	R_{rf} ($1/ft^3$)	R_{cp}($1/ft^3$)
7	3.684E+11	2.695E+11	9.887E+11	4.402E+12
15	3.684E+11	9.802E+10	7.160E+11	4.486E+12
20	3.684E+11	7.160E+11	1.571E+12	3.373E+12

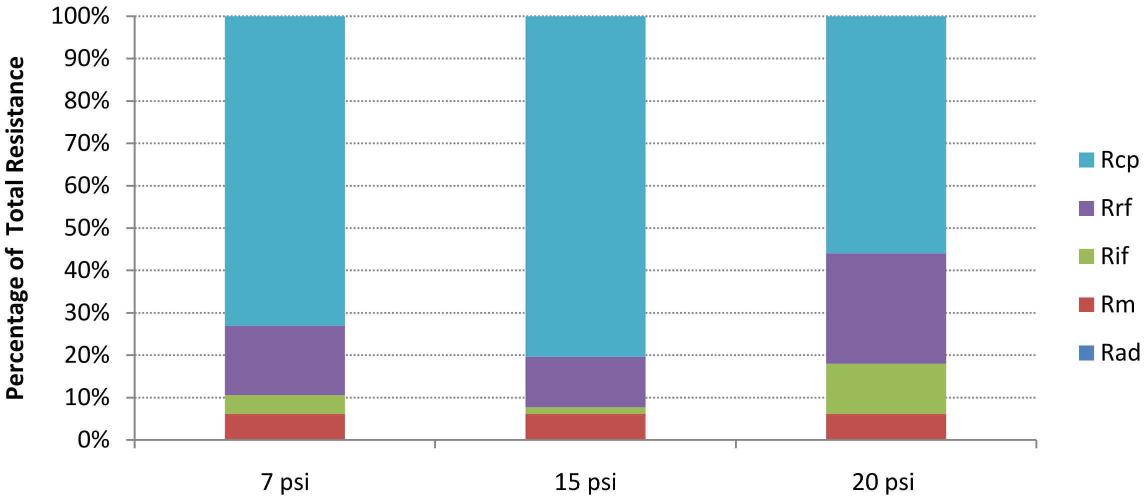


Fig. 4. 16 Proportion of the different resistances in the ceramic filtration of spent drilling. Solids concentration (8.8± 0.5% vol) and pH (9.5). Ceramic membrane pore size (0.2 micron), transmembrane pressures (7, 15 and 20 psi), cross flow velocity (10.08 ft/s) and temperature (38 C).

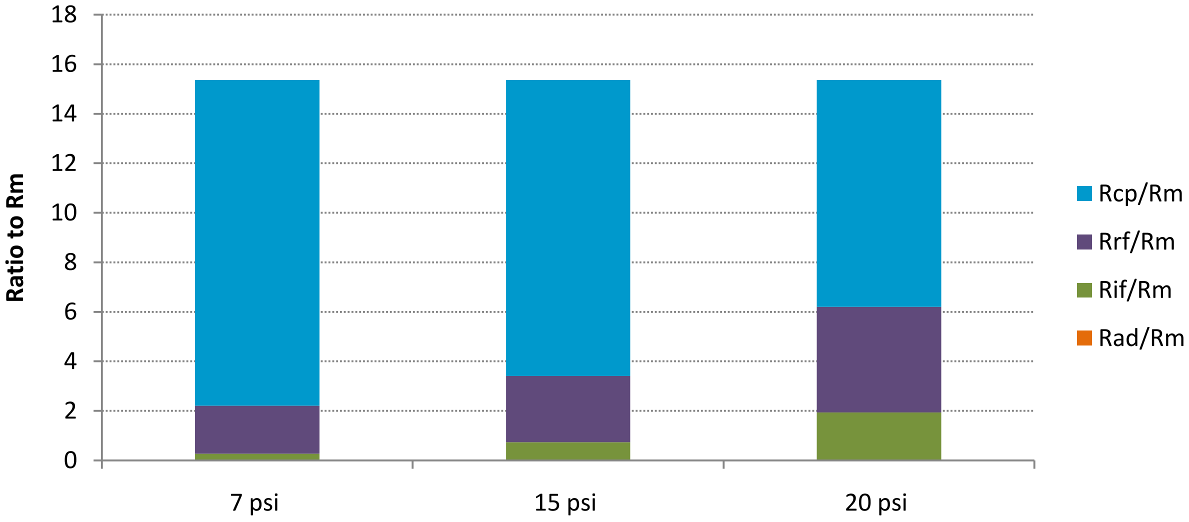


Fig. 4. 17 Ratio of the various resistances to membrane intrinsic resistance in the ceramic filtration of spent drilling fluids at different pressures. Solids concentration (8.8± 0.5% vol) and pH (9.5). Ceramic membrane pore size (0.2 micron), transmembrane pressures (7, 15 and 20 psi), cross flow velocity (10.08 ft/s) and temperature (38 C).

The resistances involved in the ceramic filtration of spent drilling fluids under different pressures are shown in figure 4.16. Increasing pressure as was seen in the filtration of spent drilling fluids caused a rapid decline in flux especially at the transmembrane pressure of 20 psi; this is corroborated by figure 4.16 showing resistances are increasing with increased pressure from the figures above. From figure 4.16 it is seen that resistance due to irreversible fouling R_{if} is largest during filtration at transmembrane pressure of 20 psi. This supports the view that at higher transmembrane pressures there is a consolidation of the fouling layer creating greater hydraulic resistance to the flow of the permeate. It is also seen that resistance due to reversible fouling R_{rf} increases with increasing pressure while concentration polarization is lowest at high pressure a possible indication of a more rapid transformation of the concentration polarization layer.

Under closer inspection of figure 4.16 it seems also that resistance due to irreversible fouling R_{if} is larger at transmembrane pressure of 7 psi when compared to transmembrane pressure at 15 psi and this seems contrary to what was observed during filtration when correlated with flux decline. Resistance due to concentration polarization also seems to be greater at transmembrane pressure of 15 psi when compared to 7 psi this intuitively seems contrary. When the resistances are plotted as a ratio of the intrinsic membrane resistance as seen in figure 4.17, the contribution of the different resistances under the different conditions becomes clearer and corroborates what was observed during filtration experiments. Resistance due to irreversible fouling is seen to increase as pressure increases and the same is also noticed for resistance due to reversible fouling. Resistance due to concentration polarization is seen to also decrease with increasing pressure.

Table 4.3. Various resistances in the ceramic filtration of spent drilling fluids at different cross flow velocities. Solids concentration (8.8±0.5% vol), pH (9.5). Ceramic membrane pore size(0.2 micron), transmembrane pressure (15 psi), cross flow velocity (6,10 and 16 ft/s) and temperature (38 C)

Cross flow velocity (ft/s)	R_m (1/ft^3)	R_{if} (1/ft^3)	R_{rf} (1/ft^3)	R_{cp}(1/ft^3)
6	3.684E+11	1.321E+11	6.310E+11	4.896E+12
10	3.684E+11	3.505E+11	6.365E+11	5.205E+12
16	3.684E+11	1.563E+11	4.537E+11	9.507E+11

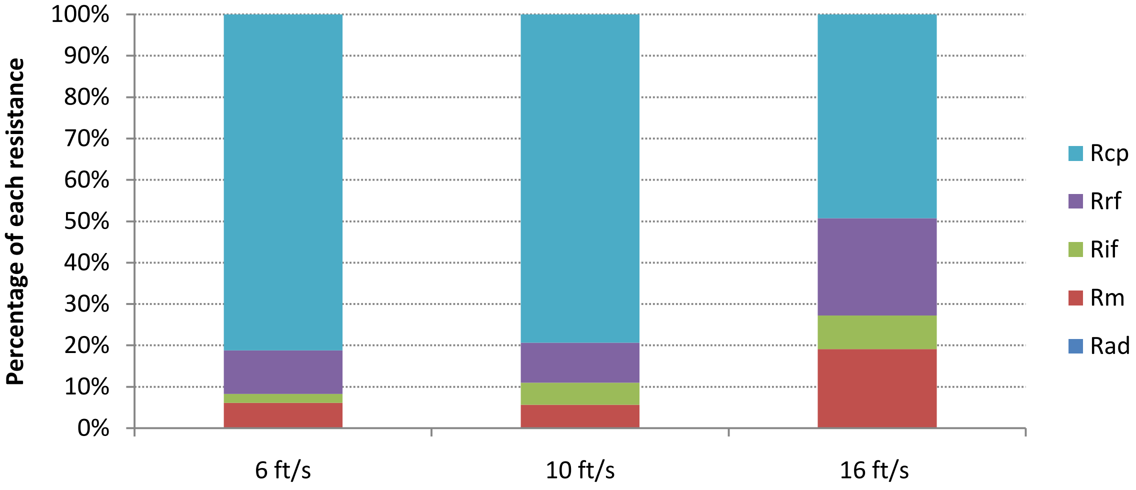


Fig. 4. 18 Proportion of the different resistances in the ceramic filtration of spent drilling fluids at various cross flow velocities. Solids concentration (8.8± 0.5% vol) and pH (9.5). Ceramic membrane pore size (0.2 micron), transmembrane pressure (10 psi), cross flow velocities (6, 10 and 16 ft/s) and temperature (38 C).

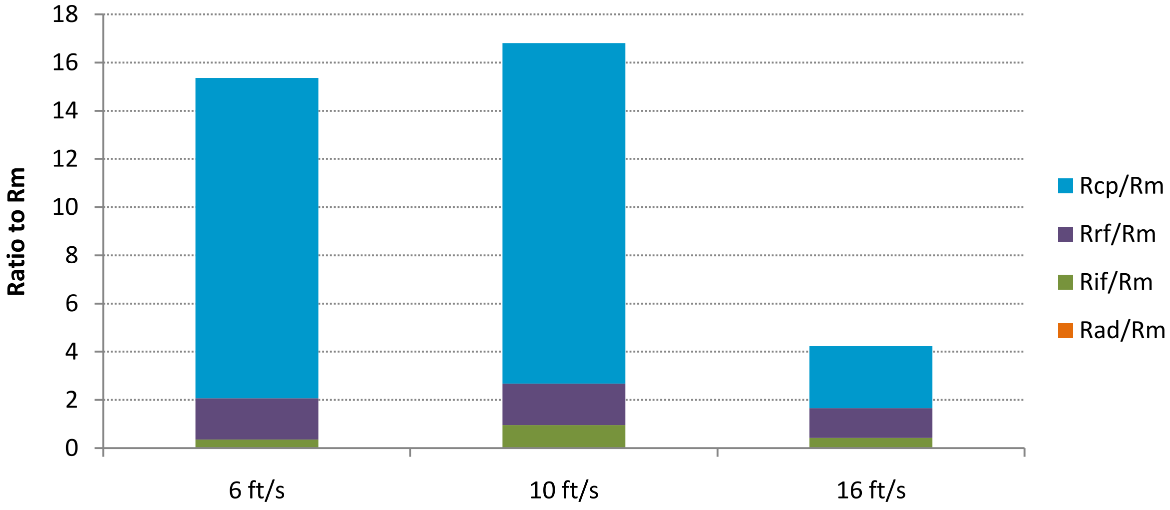


Fig. 4. 19 Ratio of the various resistances to membrane intrinsic resistance in the ceramic filtration of spent drilling fluids at different cross flow velocities. Solids concentration (8.8± 0.5% vol) and pH (9.5). Ceramic membrane pore size (0.2 micron), transmembrane pressure (10 psi), cross flow velocity (6,10 and 16 ft/s) and temperature (38 C).

The resistances involved in the ceramic filtration of spent drilling fluids under different cross flow velocities are shown in figure 4.18. With increasing cross flow velocity it seems that the resistance due to irreversible fouling increases when the percentage of the total resistance is taken into account. But when the resistances are compared to the membrane resistance it is seen that the resistance due to irreversible fouling is lowest at high cross flow velocities and similar to that at low cross flow velocity. Also it is seen that concentration polarization is also lowest at the highest cross flow velocity, this seems to support the concept of scouring of the membrane surface due to shear created by the turbulence at high cross flow velocities. The advantage of the ratio comparison to the membrane resistance is evident in the analysis of the data from different cross flow velocities. Table 4.3 shows the various resistances at different cross flow velocities.

From figure 4.19 the obvious advantages of a cross flow velocity where possible is well shown. This supports findings [64,69]that show increasing cross flow velocities were beneficial to filtration in solids laden wastes as more materials is not only passed through but the onset of flux decline is prolonged. With respect to the description of fouling as special cases of concentration polarization, from figure 4.19 it is evident that at higher cross flow velocities the change in fouling layer develops more rapidly in comparison to lower cross flow velocities. Considering the increased mass of material filtered at high cross flow velocities the rapid change in fouling layer seems intuitive and the role of pressure could also be inferred, at high pressures the change would be much more rapid. This supports the observation during the experiments at lower pressures and high cross flow velocity where the onset of flux decline was further prolonged.

Table 4.4. Various resistances in the ceramic filtration of spent drilling fluids with different solids concentration. Ceramic membrane pore size(0.2 micron), transmembrane pressure (15 psi), cross flow velocity (10 ft/s) and temperature (38 C)

Solids Concentration	R_m (1/ft^3)	R_{if} (1/ft^3)	R_{rf} (1/ft^3)	R_{cp}(1/ft^3)
Low	3.684E+11	1.521E+11	1.420E+12	5.784E+11
High	3.684E+11	1.997E+12	1.971E+12	2.2703E+12

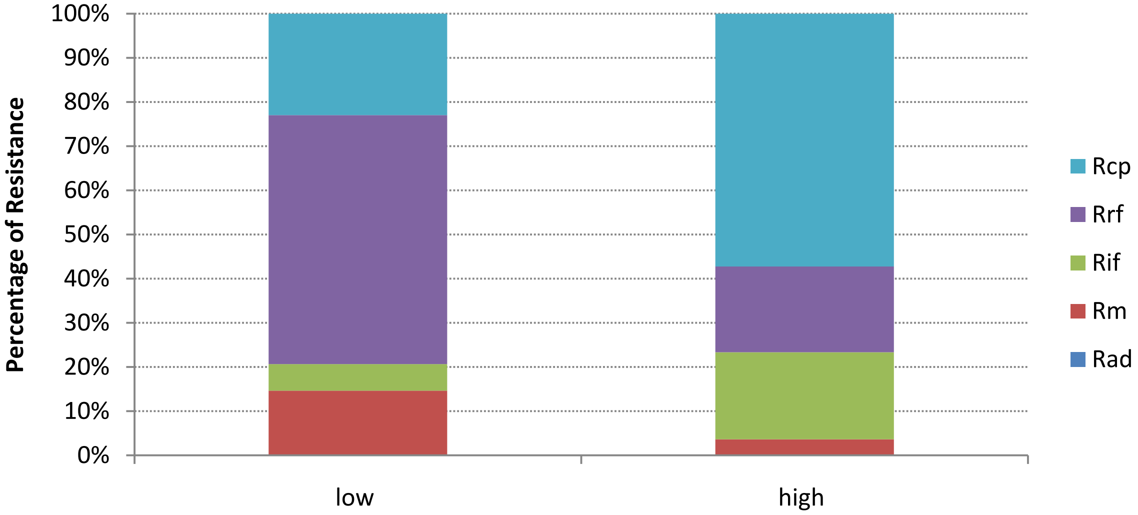


Fig. 4. 20 Proportion of the different resistances in the ceramic filtration of spent drilling fluids at various solids concentration. Solids concentration (8.8± 0.5% vol and 10.20± 0.5% vol), pH (9.5). Ceramic membrane pore size (0.2 micron), transmembrane pressure (10 psi), cross flow velocities (10 ft/s) and temperature (38 C).

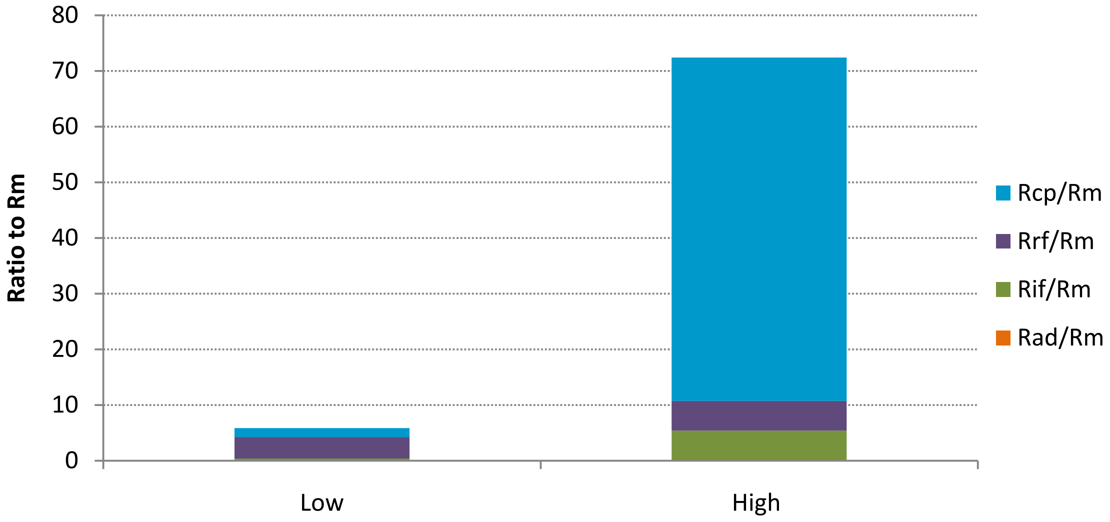


Fig. 4. 21 Ratio of the various resistances to membrane intrinsic resistance in the ceramic filtration of spent drilling fluids at different solids concentration. Solids concentration (8.8± 0.5% vol and 10.20± 0.5%) and pH (9.5). Ceramic membrane pore size (0.2 micron), transmembrane pressure (10 psi), cross flow velocity (10 ft/s) and temperature (38 C).

The resistances involved in the ceramic filtration of spent drilling fluids with different solids concentrations are shown in figure 4.20. The feed with the lower solids concentration showed a high amount of resistance due to irreversible fouling relative to other resistances in the total resistance. In the comparison to the ratio of the resistance due to the membrane, the resistance due to irreversible fouling is still significant at low solids concentration. At high solids concentration the resistance due to irreversible fouling is significant to the total resistance but lesser proportionally than what exists at low concentration. Table 4.4 shows the various resistances at different solids concentration.

When the ratio is compared to the resistance due to the membrane, the resistance ratios are the largest ratios (greater than 10, see figure 4.21) of any of the comparisons. Resistance due to irreversible fouling is 5 times the resistance due to the membrane, thus at higher solids concentration the propensity to foul is significantly greater than at any other operating parameter investigated. In the filtration of spent drilling fluids the feed concentration would be the most important characteristic in determining membrane fouling. This supports the experimental observations.

4.3.2 Resistance in series model for ceramic membrane filtration of produced water

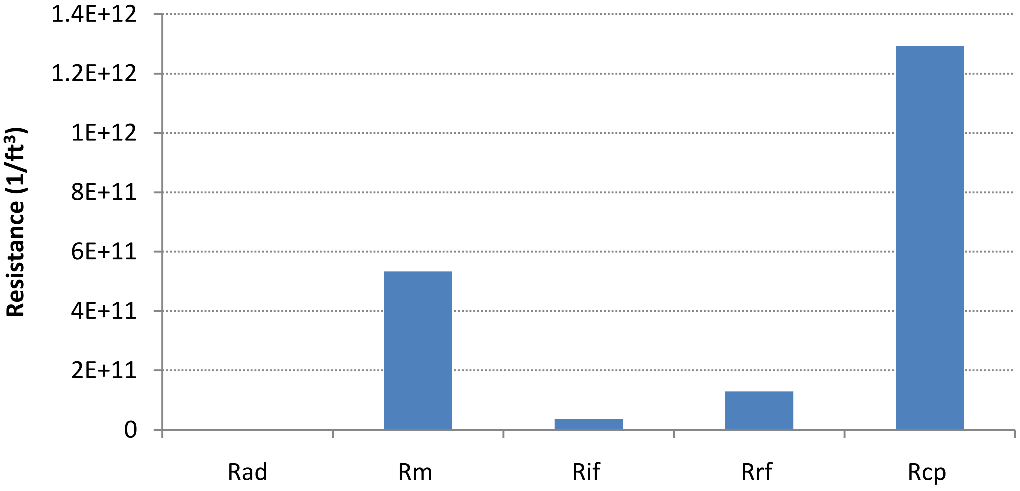


Fig. 4. 22 Different resistances in the ceramic filtration of produced water. Oil concentration 500± 200 ppm, pH 7.3± 1.5 and salinity 36,000± 5000 TDS mg/L. Ceramic membrane pore size (0.2 micron), transmembrane pressure (15 psi), cross flow velocity (8 ft/s) and temperature (38 C).

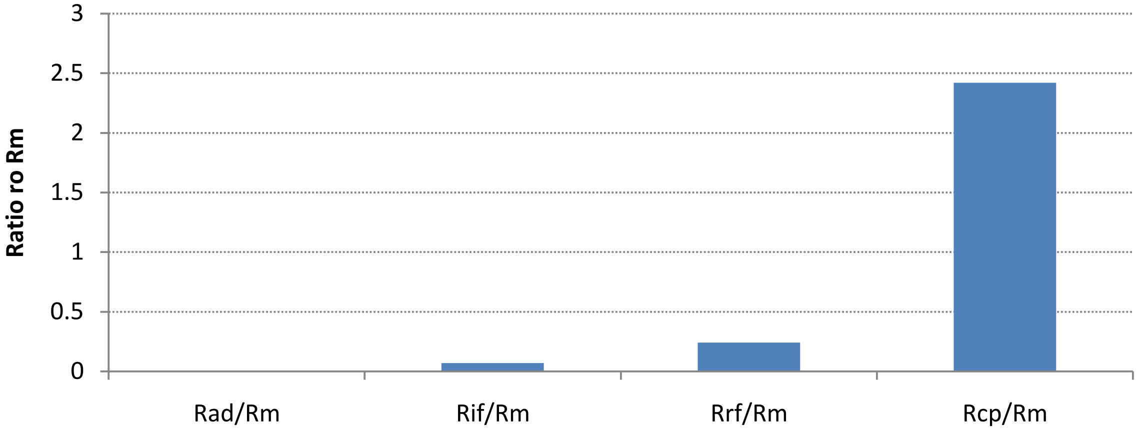
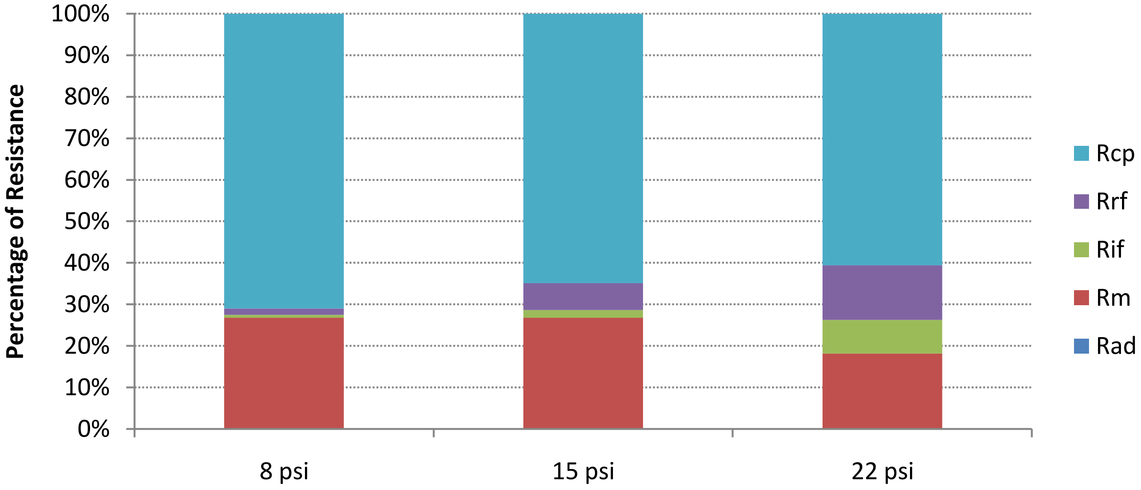


Fig. 4. 23 Ratio of the various resistances to membrane intrinsic resistance in the ceramic filtration of produced water. Oil concentration 500± 200 ppm, pH 7.3± 1.5 and salinity 36,000 ± 5000 TDS mg/L. Ceramic membrane pore size (0.2 micron), transmembrane pressure (15 psi), cross flow velocity (8 ft/s) and temperature (38 C).

The resistances involved in the ceramic filtration of produced water under the chosen arbitrary condition are shown in figure 4.22. At this condition resistance due to concentration polarization R_{cp} is the dominant resistance while the fouling resistances R_{rf} and R_{if} are significantly lesser. Intrinsic membrane resistance R_m is the second most significant resistance under this filtration condition, this is indicative of low fouling as membrane resistance is prominent in the total amount of resistance (contrast with figure 4.13). This might be indicative of a lower fouling propensity in the filtration of field produced water than of spent drilling mud. Figure 4.23 shows the ratio of the resistances to the membrane resistance. From figures 4.22 and 4.23 it is seen that resistance due to adsorption is non-existent as in the filtration of spent drilling fluids.

Table 4.5. Various resistances in the ceramic filtration of produced water at different pressures. Oil concentration 500±200 ppm, pH 7.3±1.5 and salinity 36,000±5000 TDS mg/L. Ceramic membrane pore size (0.2 micron), transmembrane pressure (15 psi), cross flow velocity (8 ft/s) and temperature (38 C)

Pressure (psi)	R_m (1/ft^3)	R_{if} (1/ft^3)	R_{rf} (1/ft^3)	R_{cp}(1/ft^3)
8	5.336E+11	3.714E+10	1.288E+11	1.292E+12
15	5.336E+11	1.431E+10	3.044E+11	1.413E+12
21	5.336E+11	2.364E+11	6.416E+10	2.101E+12



Fig, 4. 24 Proportion of the different resistances in the ceramic filtration of produced water at various pressures. Oil concentration 500± 200 ppm, pH 7.3± 1.5 and salinity 36,000± 5000 TDS mg/L. Ceramic membrane pore size (0.2 micron), transmembrane pressures (8, 15 and 22 psi), cross flow velocity (10.08 ft/s) and temperature (38 C).

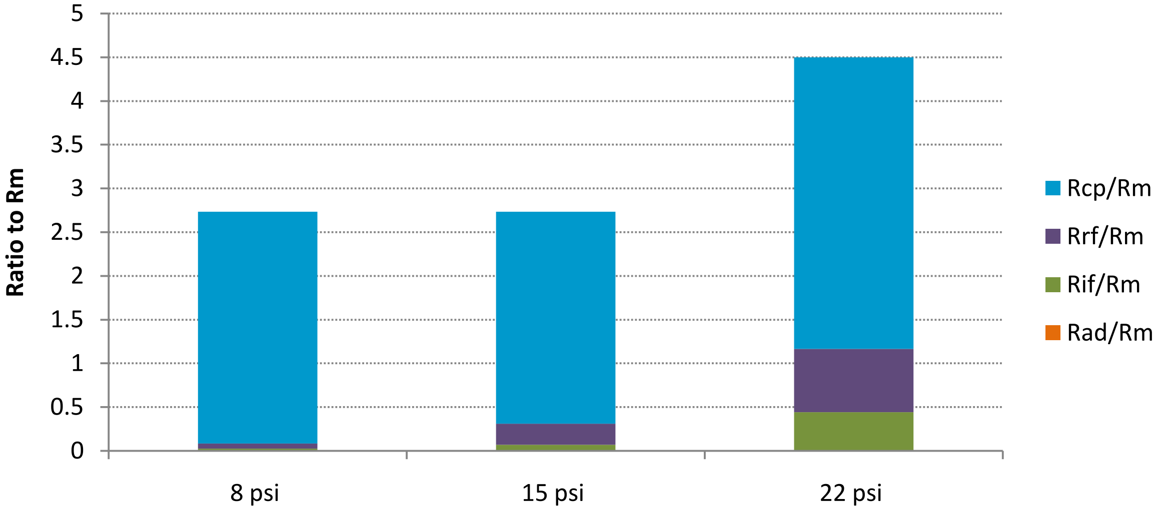


Fig. 4. 25 Ratio of the various resistances to membrane intrinsic resistance in the ceramic filtration of produced water at different pressures. Oil concentration 500± 200 ppm, pH 7.3± 1.5 and salinity 36,000± 5000 TDS mg/L. Ceramic membrane pore size (0.2 micron), transmembrane pressures (8, 15 and 22 psi), cross flow velocity (10.08 ft/s) and temperature (38 C).

The resistances involved in the ceramic filtration of produced water under different pressures are shown in figure 4.24. Increasing pressure as was seen in the filtration of produced water caused a decline in flux as higher transmembrane pressures reduced the flux (chapter III), from figures 4.24 and 4.25 increasing pressure increases the magnitude of the fouling layer. This also supports the view that at higher transmembrane pressures there is a consolidation of the fouling layer creating greater hydraulic resistance to the flow of the permeate and the resistance in series model seems to support this view. When compared with the relative magnitude of the resistances during spent drilling fluid filtration produced water filtration is smaller. In spent drilling fluid filtration there seems to be a rapid transformation of the concentration polarization layer (figure 4.17) resulting in a higher R_{rf} layer and lower R_{cp} to R_m ratio at high pressures, this transformation is not seen in produced water filtration as the R_{cp} to

R_m ratio at higher pressures is relatively similar. Table 4.5 shows the various resistances at different pressures.

Pressure is one of the most important operational factor in the reduction of permeate flux and fouling of the membrane during filtration of water based wastes. The effect of pressure is more pronounced in filtration of wastes with higher solids concentration than with lower solids concentration. Pressure is also significant to flux values and thereby the productivity of the membrane filtration process. Low pressures though reducing the flux decline and fouling propensities would bring about low flux making filtration uneconomical. Thus a balance needs to be developed between the filtration pressure and fouling and flux decline propensities, and good cleaning or anti-fouling practices are an essential part of this balance.

Table 4.6 Various resistances in the ceramic filtration of spent drilling fluids at different cross flow velocities. Oil concentration 500±200 ppm, pH 7.3±1.5 and salinity 36,000±5000 TDS mg/L. Ceramic membrane pore size(0.2 micron), transmembrane pressure (15 psi), cross flow velocity (5,8 and 13 ft/s) and temperature (38 C)

Cross flow velocity (ft/s)	R_m (1/ft^3)	R_{if} (1/ft^3)	R_{rf} (1/ft^3)	R_{cp}(1/ft^3)
5	5.336E+11	1.660E+11	8.873E+11	5.719E+11
8	5.336E+11	3.714E+11	1.288E+11	1.292E+11
13	5.336E+11	1.547E+11	5.584E+11	4.959E+11

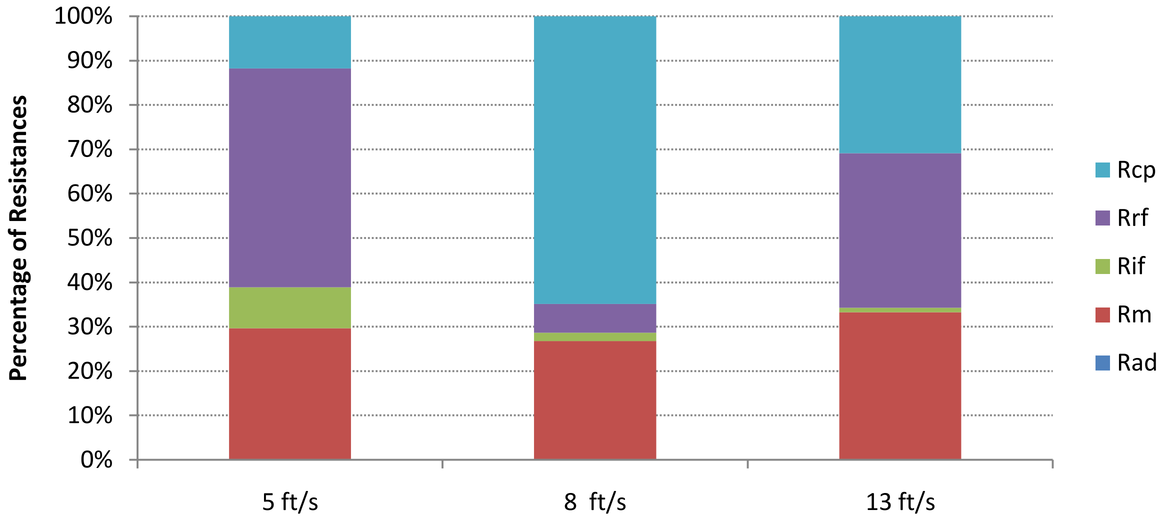


Fig. 4. 26 Proportion of the different resistances in the ceramic filtration of spent drilling fluids at various cross flow velocities. Oil concentration 500± 200 ppm, pH 7.3± 1.5 and salinity 36,000± 5000 TDS mg/L. Ceramic membrane pore size (0.2 micron), transmembrane pressure (10 psi), cross flow velocities (5, 8 and 13 ft/s) and temperature (38 C).

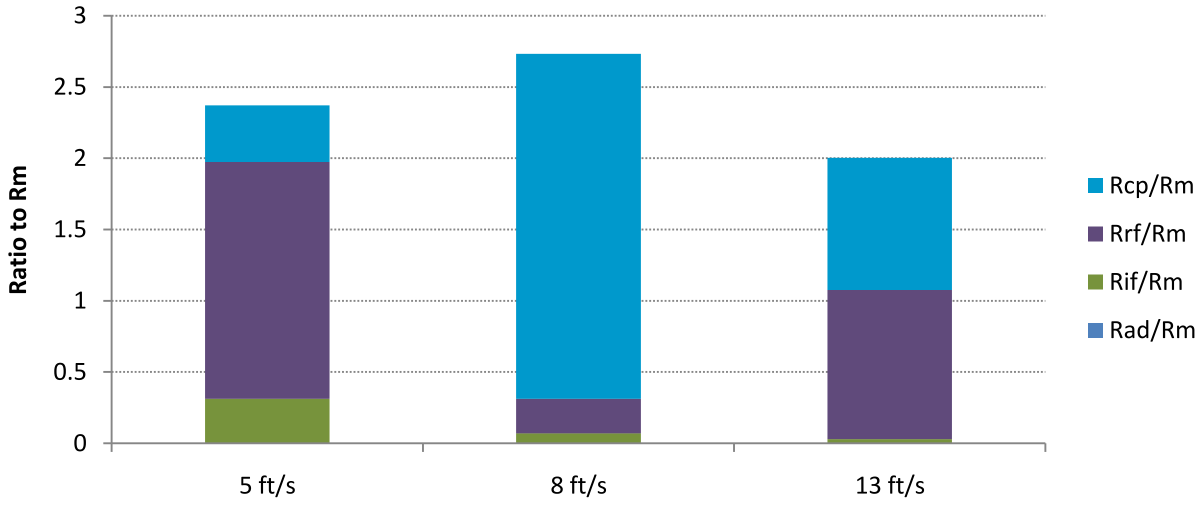


Fig. 4. 27 Ratio of the various resistances to membrane intrinsic resistance in the ceramic filtration of spent drilling fluids at different cross flow velocities. Oil concentration 500± 200 ppm, pH 7.3± 1.5 and salinity 36,000± 5000 TDS mg/L. Ceramic membrane pore size (0.2 micron), transmembrane pressure (10 psi), cross flow velocities (5, 8 and 13 ft/s) and temperature (38 C).

The resistances involved in the ceramic filtration of produced water under different cross flow velocities are shown in figure 4.26 and 4.27. The resistances show no clear patterns as the cross flow velocity decreases or increases except that resistance due to reversible fouling decreases as cross flow velocity decreases (figure 4.27). At the lowest cross flow velocity (5 ft/s) there is a rapid change of the concentration polarization layer (much greater than at high pressure) layer and a high magnitude of resistance due to both reversible and irreversible fouling. At the highest concentration where it is expected that fouling layer be minimal, the ratio of R_{cp} to R_m and R_{rf} to R_m are relatively large when compared to filtration of spent drilling fluids under similar conditions. Table 4.6 shows the various resistances at different cross flow velocities.

This observation seems to support the theory that with feeds with low solids concentration such as produced water the advantage of high cross flow velocities is measured relative to feeds with high cross flow velocities. Or more narrowly focused, it is observed that high cross flow velocities is not very effective during filtration as a flux decline mitigation tool in low solids feed. The low solids concentration and particle size distribution do not create enough shear for the scouring of the membrane surface to prolong the onset of hydraulic resistance to the permeate flow. This is also evidence to show that turbulence generated by the flow through the membrane is aided by the solids concentration in controlling flux decline in ceramic filtration of spent drilling fluids. This resistance observation at different cross flow velocities during produced water filtration could also be indicative of the dominant fouling mechanism during filtration. If cake layer formation were the dominant mechanism, without pressure interference, cross flow velocity should affect the resistances significanlty; this observation seems to lend credence to pore plugging as the dominant fouling mechanism in produced water filtration.

Table 4.7 Various resistances in the ceramic filtration of produced water with different oil concentrations. Ceramic membrane pore size(0.2 micron), transmembrane pressure (15 psi), cross flow velocity (8 ft/s) and temperature (38 C)

Oil concentration	R_m (1/ft^3)	R_{if} (1/ft^3)	R_{rf} (1/ft^3)	R_{cp}(1/ft^3)
Low	5.336E+11	3.714E+10	1.288E+11	1.292E+12
High	5.336E+11	1.170E+11	1.277E+12	1.870E+12

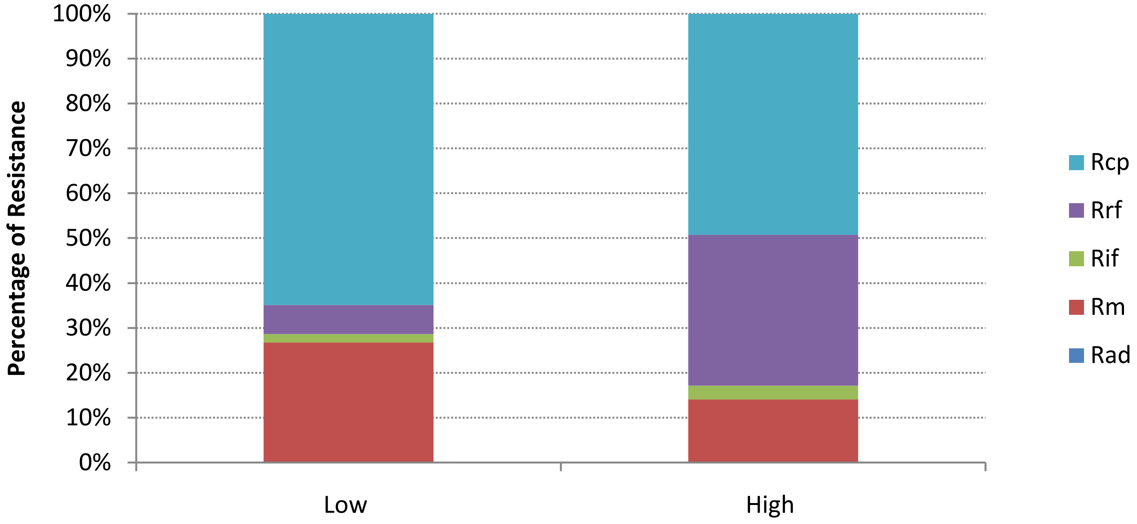


Fig. 4. 28 Proportion of the different resistances in the ceramic filtration of produced water at various oil concentrations. Oil concentration 500± 163 ppm (low) and 1200± 186 ppm , pH 7.3 ± 1.5 and salinity 36,000± 5000 TDS mg/L. Ceramic membrane pore size (0.2 micron), transmembrane pressure (10 psi), cross flow velocities (15 ft/s) and temperature (38 C).

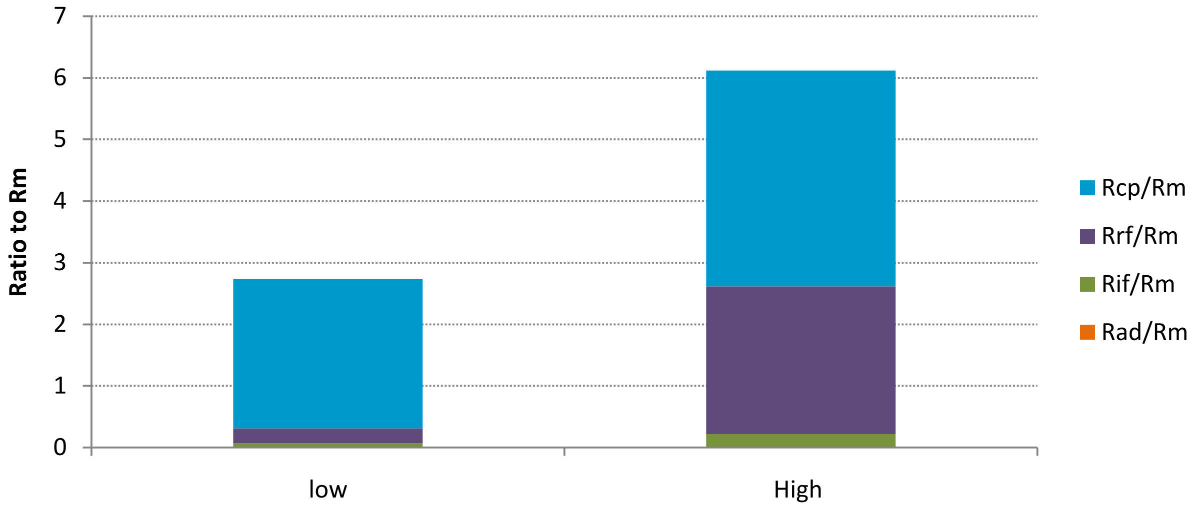


Fig. 4. 29 Ratio of the various resistances to membrane intrinsic resistance in the ceramic filtration of produced water at various oil concentrations. Oil concentration 500± 163 ppm (low) and 1200± 186 ppm , pH 7.3± 1.5 and salinity 36,000± 5000 TDS mg/L. Ceramic membrane pore size (0.2 micron), transmembrane pressure (10 psi), cross flow velocities (15 ft/s) and temperature (38 C).

The resistances involved in the ceramic filtration of spent drilling fluids with different solids concentrations are shown in figure 4.28 and 4.29. As expected the fouling resistances increased with increasing oil concentration in the feed though it is observed that the resistance due to irreversible fouling is not as significant proportionally to other resistances. The magnitude of the resistances also differs significantly when the solids concentration in the spent drilling fluids is increased than when the oil concentration in produced water is increased. The magnitude of resistances in high solids concentration in drilling mud (60 to 1, R_{cp} to R_m; 6 to 1 R_{cp} to R_{rf} and 7 to 1 R_{cp} to R_{if}) are significantly higher than in high oil concentration in produced water (4.5 to 1, R_{cp} to R_m; 2.5 to 1 R_{cp} to R_{rf} and 0.2 to 1 R_{cp} to R_{if}). Table 4.7 shows the various resistances at different oil concentrations.

It is intuitive that increasing feed concentration parameters would increase not only the flux decline but also the fouling propensity. Investigation into feed parameter variation is most useful in the determination of the optimal feed characteristic for filtration and for fouling studies. Practically, filtration is better optimized at low feed concentrations but this would have to be weighed against feasible flux objectives for filtering the feed. In this study for the feed parameters of solids concentration in spent drilling fluids and oil in produced water, the upper limits of what are practically obtainable were used in our study, thus it is expected that if pre-treatment methods are upstream of the membrane filtration better filtration results would be produced above that which is reported here.

Hollow fibre

Determining the resistances with the hollow fibre membrane was not practical. Hollow fibre membranes due to their low pressure and low cross flow velocity did not affect the resistance calculations to make much of a difference thus it was hard to apply the resistance in series model. Pressure changes are important to the resistance calculation, after determining the fouling period of the hollow fibre membranes pressure differences were not substantial for the equations to be valid. The same applied to cross flow variation where the range was small and the difference in flux not stark in hollow fibre membrane filtration (chapter III).

4.4 Summary

Though there are a plethora of models aimed at describing the filtration of a feed, it is rather difficult to predict with measurable certainty the filtration of most feeds. Empirical data still remains the best method to adequately understand the filtration pattern of the feed. In this chapter the simplified model used was not adequate in predicting the filtration pattern observed when fitted with actual data experiments. It was also difficult to determine the exact mechanism of flux decline as no individual mechanism fully explained the flux decline as the mixture of mechanisms seemed to exist. Though no mechanism rightly explains the flux decline, if fouling is due to physical means the probable reason would be due to either pore plugging or cake formation or a mixture of both of them.

The approach taken in calculating resistance served a central purpose of helping to develop a practical tool in the analysis of membrane integrity during use. Most membrane resistance calculations are done mostly as academic enterprises to explain the different interactions that exist during filtration. The resistance model chosen for calculation resistance was used due to its simplicity and its utility in being an actual tool for the monitoring of membrane integrity during actual operations. Using pressure reading and flux calculation, the membrane state can always be determined by comparing it to its intrinsic membrane resistance. A simplified excel program was developed to show (appendix) how an operator either during field pilot programs or actual membrane systems can apply this model to monitor the membrane behavior. More advanced systems can be automated to have this utility.

CHAPTER V

FOULING MITIGATION AND MEMBRANE CLEANING

5.1 Introduction

In the last chapter ways to predict the filtration profile in the ceramic and hollow fibre membrane filtration of water based wastes was examined, no suitable models could aptly describe the filtration pattern adequately. Determining the propensity of fouling through resistance calculation was also investigated and it was determined that it could be used as a simple practical tool in long term membrane integrity monitoring. Knowing the filtration pattern or resistance build-up during membrane filtration is in itself not an end, methods must be devised that address flux decline and membrane fouling for continued filtration. If a kmembrane system cannot be effectively cleaned and maintained then using membranes should be dissuaded. In this chapter two issues are examined, one, the fouling mitigation technique called backwashing and two, membrane cleaning. This chapter reports on the investigation of backwashing in the ceramic filtration of both spent drilling fluids and produced water and in the hollow fibre filtration of produced water.

As explained in previous chapters flux decline is an inevitable reality in the filtration of any feed that is not ideal (i.e. free of solutes), another reality is that despite rigorous fouling mitigation methods membrane fluxes over time shall decrease. Membrane fouling by minerals, organics, particles, colloids and microbial growth is a major operational concern that warrants periodic membrane cleaning [72,73]. Though flux recovery is possible employing fouling mitigation techniques the subtle accumulation of solutes not removed during mitigation techniques shall increase with time and increasingly intrinsic membrane resistances shall be larger.

To combat flux decline during actual filtration and to arrest gradual membrane integrity decline over time backwashing and chemical membrane cleaning are respectively used to address these issues. In the previous chapter some form of membrane washing was introduced where pure water was used in flushing the membrane at high cross flow velocity and low pressure. Also introduced was the idea of irreversible fouling i.e. fouling that cannot be addressed using operational parameters, to address irreversible fouling or fouling due to chemical interactions membrane cleaning using cleaning materials was investigated to regain flux.

Backflushing involves the flushing of clean permeate/ solids free effluent in reverse direction of the flow of permeate through the membrane outer skin at higher cross flow velocities and low pressure for a brief period during filtration. During filtration using a different pump or the same pump, clean water of solids free permeate is forced in reverse direction to the filtration flow of the permeate dislodging the solutes stuck in the pore spaces from outside. Backflushing forces the clean permeate/solids free effluent from the outer skin of the membrane through the pores to the lumen of the membranes. Terminologies in explaining this concept varies from author to author sometimes backflushing is called backpulsing, backflushing was not investigated but backwashing.

Backwashing involves the flow of clean permeate/solids free effluent in reverse direction of the feed flow through the membrane lumen i.e. the same passage way the feed passes through the membrane. Backwashing happens at higher cross flow velocity than the filtration cross flow velocity and also at lower pressure than the filtration pressure. Backwashing and backflushing are similar in that they occur at higher cross flow velocities than filtration cross flow velocities and they use clean permeate/ solids free effluent. They differ in where the flow is reversed from; backwashing flow is reverse to the feed flow i.e. from the outlet end to the inlet end while backflushing flow is reverse to the permeate flow i.e. from the membrane outer skin to the membrane inner skin.

Backwashing i.e. the reverse flow of the feed is believed to be most effective at the dealing with the concentration polarization layers at the membrane surface and in cases of high shear can unplug pore spaces. At higher cross flow velocity the turbulence of the solids free stream dislodges the cake filter layer at the surface of the membrane thereby reducing hydraulic resistance to the flow of permeate. Backflushing i.e. the reverse flow of the permeate is believed to be most effective at dealing with pore plugging, flow unplugs the pores from the outer layer but the pressure should exceed the pressure of the filter cake (if it exists). At high enough pressure during backflush the force through the pores if high enough should be able to dislodge the solute particles and free the pore space and the filter cake. Both techniques address fouling or flux decline issues that are of a physical nature.

As discussed inevitably chemical interactions between solutes in the feed and the membrane would cause some fouling and this fouling cannot be remedied by using any physical process. This type of fouling also includes what was termed irreversible fouling in the last chapter and fouling due to membrane interactions with the feed. Since extensive chemical characterization of the feed was not carried out due to the variability of the feed, it would be impossible to adequately know precisely the chemical nature of the contaminants causing the fouling. This makes it difficult to apply a particular or specific cleaning agent to cleaning the membrane. In situations where the feed is properly characterized the nature of its constituents gives an indication of the chemical nature of the interaction with the membrane. Chemicals that are capable of neutralizing or changing the nature of this interaction are employed to effectively clean the membrane and they are for most part effective. Typical cleaning agents for membrane cleaning are acids, bases, enzymes, surface active agents, detergents, sequestering agents and disinfectants [75].

The approach in this thesis takes a broader part since the luxury of characterizing the wastes is non-existent. The broader approach adopted was a cleaning solution that involved both alkaline and acidic wash and another cleaning solution that is a micellar solution, both solution types were investigated. The cleaning solution that involves an acidic and alkaline wash would address a broad range of chemical interactions between the membrane and the feed while the micellar solution would give insight into cleaning with primarily surfactants. The flux recovery was calculated based on the difference between the flux after fouling and cleaning to the flux before fouling.

5.2 Fouling Mitigation Technologies

5.2.1 Ceramic Filtration of Spent Drilling Fluid

The spent drilling fluids used in these set of experiments were defined to have 8.8± 0.5% solids (`19,000 mg/L) and a pH of 9.5± 0.3 and the initial feed volume was 8 gallons and the experiment run in recycle mode. Arbitrary operating parameters for ceramic filtration for fouling mitigation experiments were cross flow velocity of 12 ft/s, transmembrane pressure of 12 psi and temperature of 38 C. During backwashing was initially applied every 15 minutes for 5 seconds at a cross flow velocity of 18 ft/s from an external pump, this was then changed to every 40 minutes to better address flux decline. The flow from the wash was collected outside the system and not reintroduced into the system. The experiments were repeated twice and the result shown is an average of the fluxes, the reproducibility of the experiments was high.

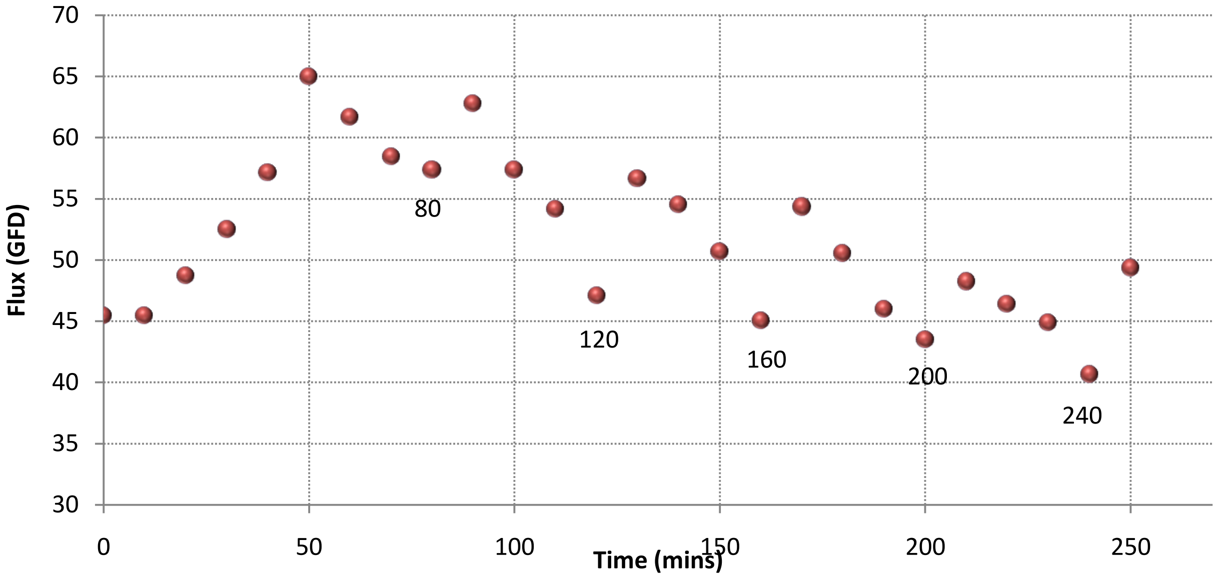


Fig. 5. 1 Backwashing in the filtration of spent drilling fluids using ceramic membranes. Solids concentration (8.8± 0.5% vol) and pH (9.5). Ceramic membrane pore size (0.2 micron), transmembrane pressure (15 psi), cross flow velocity (12 ft/s) and temperature (38 C). Backwash cross flow velocity (18 ft/s), backwash duration (30 secs), backwash interval (40 minutes).

In the filtration of spent drilling fluid to see the effect of fouling mitigation technologies, the investigation was initially carried out with backwashing every 15 minutes for one hour. The result showed no significant difference from initial filtration experiments because during the experiment duration there was no significant drop in the flux. After 40 minutes of filtration it was noticed that flux decline was imminent, new experiments were designed to filter longer (four hours) and to have backwashing every 40 minutes. The backwashing regimen included washing with solids free effluent for 30 seconds in the reverse flow of filtration at low pressure and high cross flow velocity of 18 ft/s using an external pump. The initial volume used for backwashing was made up with some reverse osmosis water to make up for the needed volume. Figure 5.1 is an average of two individual runs and both runs showed a high degree of reproducibility.

From the filtration of spent drilling fluid with 8.8± 0.5% solids (~ 19,000 mg/L) and a pH of 9.5± 0.3, filtered at 12 ft/s at 15 psi and 38 C with five episodes of backwashing at the 80th, 120th, 160th, 200th and 240th interval the average flux was 51.67 GFD, maximum flux was 64.98 GFD and the minimum flux was 40.66 GFD. The traditional "hump" (rise in flux) noticed in spent fluids filtration occurs till the 50th minute, the cross flow velocity is higher than the arbitrary cross flow velocity used in earlier experiments (12 ft/s vs 10.08 ft/s) and this explains the additional rise in the hump. There is no backwash added in the initial hour of filtration till the 80th minute. At the 80th minute the flux is 57.3 GFD, after the first backwash the flux jumps up to 62.7 GFD, about 10% rise from the last flux before backwashing and just about 3% less than the initial highest recorded flux, this would represent a flux recovery of about 97%. With about 97% recovery of the flux in the initial 80 minutes of filtration it could be assumed that the mechanism of blocking most dominant at this point would be cake layer formation.

In the next 40 minutes (80th -120th) of filtration we see a decline in the flux from its zenith after the first backwashing from 62.7 GFD to 47.1 GFD representing 20% decline in the flux which is about the normal flux decline in the previous ceramic filtration of spent drilling fluid experiments. At 120 minutes another backwash is carried out at the same regimen i.e. 30 seconds with solids free permeate at high cross flow velocity of 18 ft/s and low pressure. At the 120th minute the flux is 47.1 GFD and after the backwash the flux jumps up to 56.7 GFD, about 20% rise from the last flux before backwashing and 13% less than the initial highest recorded flux, this would represent a flux recovery of about 87%. Backwashing at this stage is still rather effective and though the flux rise after backwashing is higher than the initial backwash, overall 10% of the original highest flux is lost after the initial backwash and this is still less than the 20% flux decline observed in previous filtration experiments using the same feed characteristics.

During the next 40 minutes (120th -160th) of filtration we see a decline in the flux after the second backwashing from 56.6 GFD to 45.0 GFD representing 20% decline in the flux which is about the normal flux decline in the previous ceramic filtration of spent drilling fluid experiments. After the backwash at the 120th minute mark the flux climbs up from 45.03 GFD to 54.3 GFD, about 20% rise from the last flux before backwashing and 17% less than the initial highest recorded flux, this would represent a flux recovery of about 83%. The flux pattern at this stage of the third backwash is similar to the second backwash and it is seen that with increasing amount of backwashing and time flux recovery with respect to the highest flux decreases subtly. At this stage backwashing is still an effective fouling mitigation technique.

During the next 40 minutes (160th -200th) of filtration we see a decline in the flux after the second backwashing from 54.3 GFD to 43.5 GFD representing 20% decline in the flux which is about the normal flux decline in the previous ceramic filtration of spent drilling fluid experiments. After the backwash at the 200th minute mark the flux climbs up from 43.5 GFD to 48.2 GFD, about 10% rise from the last flux before backwashing and 26% less than the initial highest recorded flux, this would represent a flux recovery of about 74%. The flux pattern at this stage differs from the last two backwash cycles as the flux gain after backwashing is halved (10%) and the flux after backwashing fell below 20% of the initial highest recorded flux. The final backwash is carried out at the 240th minute and the flux rises from 40.7 GFD to 49.4 GFD representing a 20% rise in flux and a 24% loss of the highest reported flux. In this backwash we see the resumption to gaining 20% of the flux decline after backwash but it seems that the 20% of the highest recorded flux is lost to irreversible fouling.

Backwashing in the filtration of spent drilling fluid was effective in maintaining the flux within the duration of the filtration experiments. The permeate gain by having the flux maintained with backwashing was significant. Comparing the total permeate resulting from the experiments during resistance calculation where there was no backwashing and the backwashing experiment, backwashing gave 54% more permeate for the same duration than when not using backwashing. The backwashing interval chosen (40 minutes) was to show the effect of backwashing, using earlier intervals would have better maintained the flux and increased the gain on the total permeate volume. But increasing the backwash frequency would also have a bearing on the volumes needed for backwashing as significant volumes might be needed to backwash actual systems thereby reducing the available permeate if the permeate is the intended product. Process design of larger system would have to investigate an appropriate balance between the frequency of backwashing and its practicality in the face of filtration endpoints.

The effectiveness of backwashing in addressing the flux decline might be pointing towards cake filtration formation as a dominant membrane blocking mechanism during the operational filtration of spent drilling fluids. Using the Hermia models in chapter IV, the correlation with the cake filtration blocking mechanism was high as well as with other mechanisms such as pore plugging. Backwashing intuitively seems more effective against cake filtration but if enough shear is generated there might be enough to dislodge particles from pore spaces after the removal of the cake filter or in situations where the depth of the plugged pores are superficial. During the first three backwash cycles the percentage gain in the flux was significant though the gain was halved on the fourth backwash, this could be due to plugging of some membrane pores due to incremental deposition into the pores each time the wall is formed.

In conclusion the advantage of fouling mitigation techniques such as backwashing is primarily to prevent significant flux decline during filtration, and this was achieved during the filtration of spent drilling fluids but its effect in reducing the resistances in membrane filtration was mild. It would have seemed intuitive that in reducing the fouling using fouling mitigation techniques this would also reduce the need for cleaning or the amount of total fouling experienced by the membrane. In the end it is seen that the final flux loss is close to what would have obtained if there were no backwash i.e. about 20% loss in the flux overall, this seems to suggest that the fouling mitigation technique is impotent against irreversible fouling. This also seems to suggest that mechanism of fouling or blocking cannot be explained solely by one mechanism for example cake layer formation, that realistically a combination of blocking or filtration mechanism is at play. The major advantage with backwashing is the ability to filter longer and the increase in permeate volume due to longer filtration.

5.2.2 Ceramic Filtration of Produced Water

The produced water used in these set of experiments were defined to have an oil concentration of 700± 200 ppm, pH 7.3± 1.5 and salinity 36,000± 5000 TDS mg/L. Arbitrary operating parameters for ceramic filtration was cross flow velocity of 8 ft/s, transmembrane pressure of 15 psi and temperature of 38 C. During filtration backwashing was applied every 25 minutes for 30 seconds at high cross flow velocity of 16 ft/s from an external pump. The flow from the wash was collected outside the system and not reintroduced into the system. The experiments were repeated twice and the result shown is an average of the fluxes, the reproducibility of the experiments was high.

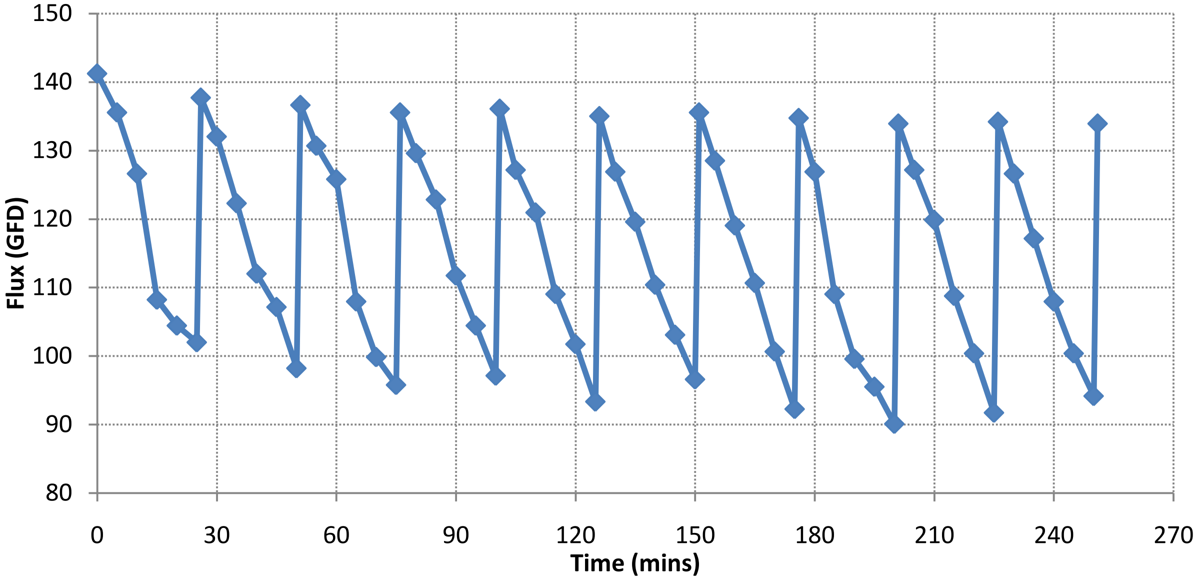


Fig. 5. 2 Backwashing in the filtration of produced water using ceramic membranes. Oil concentration 700± 200 ppm, pH 7.3± 1.5 and salinity 36,000± 5000 TDS mg/L. Ceramic membrane pore size (0.2 micron), transmembrane pressure (15 psi), cross flow velocity (8 ft/s) and temperature (38 C).

The average flux was 115.58 GFD, maximum flux was 141.25 GFD and the minimum flux was 90.10 GFD. The flux decline in the filtration of produced occurs usually after about twenty minutes filtration from previous experiments, this informed the decision to make backwash every twenty five minutes. Before the initial backwash the flux had dropped to 30% of the initial flux volume, after the backwash 96% of the initial flux was recovered. In the next 25 minutes following the initial backwash the flux would also fall below 30% of the initial flux and after backwash 95% of the initial flux was regained. This was repeated throughout the duration of the experiment. The lowest flux gain was 93% of the initial flux and that was after more than four hours of operation. After operation the clean flux after filtration was 94% of the original clean water flux before filtration.

Backwashing is an effective fouling mitigation technique in the filtration of produced water. Backwashing at the interval produced the intended objective of regaining the flux well within initial flux range. Unlike backwashing during the filtration of spent drilling fluids where the flux gained after backwashing reduced progressively with time, the loss of flux with backwashing in ceramic filtration of produced water was negligible. Although the intervals of backwash differed the relative gain after backwash is far less in the filtration of spent drilling fluid compared to produce water backwash.

Also the proportion of the membrane lost to irreversible fouling differed significantly; in the filtration of spent drilling fluid about 20% of the membrane is lost to irreversible fouling while in the filtration of produced water just about 6% of the membrane is lost to irreversible fouling. Thus it would be expected in the filtration of produced water that less chemical treatment shall be afforded the membrane. Not only is the irreversible fouling proportion reduced in the backwashed membrane the permeate volume is about five times the permeate volume if the membrane was not backwashed.

The effectiveness of backwashing during produced water filtration allows some inferences about the nature of the mechanism of fouling or the nature of the fouling layer. The near complete flux gain after backwashing in the filtration of produced water is indicative of either the cake layer that is formed is completely removed by the backwashing or pore plugging is not a major blocking mechanism or that the backwashing at the cross flow velocity also addresses pore plugging. This might indicate that the reduction in flux gain after backwashing in spent drilling fluid filtration could either be due to the fact that the cake layer is not completely removed during backwashing or there is pore plugging at some level during filtration. These differences in the amount of recovery flux depict the complexities involved in membrane-feed interaction and how they affect membrane fouling and filtration.

5.2.3 Hollow Fibre Filtration of Produced Water

The produced water used in these set of experiments were defined to have an oil concentration of 500± 200 ppm, pH 7.3± 1.5 and salinity 36,000± 5000 TDS mg/L. Higher oil concentration (but less that 700 ppm) was used as low oil concentrations less than 200 ppm had minimal flux decline. Arbitrary operating parameters for ceramic filtration were cross flow velocity of 3.38 ft/s, transmembrane pressure of 8 psi and temperature of 38 C. During filtration backwashing was applied every 15 minutes for 30 seconds at high cross flow velocity of 7 ft/s and low pressure from an external pump. The manufacturer's limitation on pressure informed the lower pressure for filtration so that membrane transmembrane pressure could rise to 15 psi during backwash. Also the backwash cross flow velocity was limited to 7 ft/s due to the limitation of the allowable cross flow velocity. The flow from the wash was collected outside the system and not reintroduced into the system. The experiments were repeated twice and the result shown is an average of the fluxes, the reproducibility of the experiments was high.

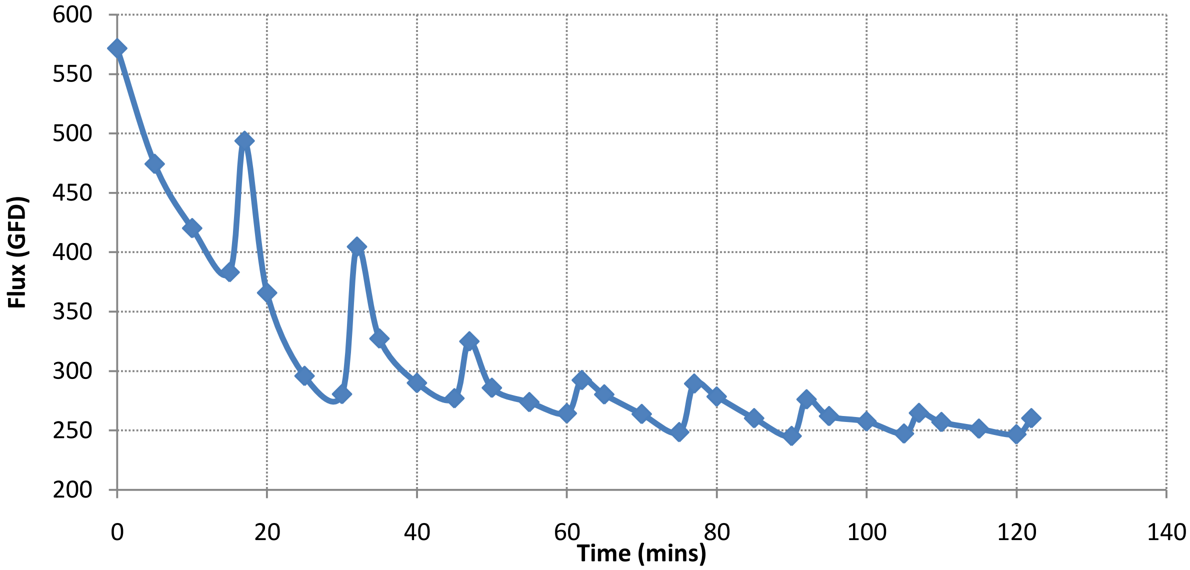


Fig. 5. 3 Backwashing in the filtration of produced water using hollow fibre membranes. Oil concentration 500± 200 ppm, pH 7.3± 1.5 and salinity 36,000± 5000 TDS mg/L.. Ceramic membrane pore size (0.2 micron), transmembrane pressure (8 psi), cross flow velocity (3.8 ft/s) and temperature (38 C).

The average flux was 309.6 GFD, maximum flux was 571.8 GFD and the minimum flux was 246.7 GFD. A sample with a higher oil concentration was filtered in the fouling mitigation study with the hollow fibre membrane to determine if backwash could be an effective method in the reducing fouling in the filtration of samples with high oil concentrations. This explains why the oil content was higher than what obtained in the arbitrary concentration set. Flux decline was most apparent after 15 minutes and this informed the backwash time after 15 minutes. Before the initial backwash the flux had dropped to 33% of the initial flux volume, after the backwash 86% of the initial flux was recovered. This was less than 96% in the filtration of produced water with similar oil content using ceramic membranes.

The next backwash 30 minutes into filtration raised the flux from 280.5 GFD to 404.7 GFD; this was 11% less than highest flux before the second backwash and 30% less than the original highest flux at the beginning of the experiment. The next backwash 45 minutes into filtration raised the flux from 277.1 GFD to 325 GFD; this was 20% less than highest flux before the third backwash and 43% less than the original highest flux at the beginning of the experiment. The next backwash 60 minutes into filtration raised the flux from 264.4 GFD to 292.3 GFD; this was 11% less than highest flux before the fourth backwash and 50% less than the original highest flux at the beginning of the experiment. The next backwash 75 minutes into filtration raised the flux from 248.5 GFD to 289.4 GFD; this was 3% less than highest flux before the fifth backwash and 50% less than the original highest flux at the beginning of the experiment. From this point the backwashing does not increase the flux within 50% of the original flux and the effect of backwashing is nominal and in both trials the experiment is discontinued.

Backwashing is seen to be an ineffective fouling mitigation technique in the filtration of produced water using hollow fibre membranes. Backwashing at the interval used in these experiments did not produce the intended objective of regaining the flux or keeping the flux within 50% of the original initial flux. Unlike backwashing during the ceramic filtration of produced water where the flux gained after backwashing was slightly below the initial, the loss of flux with backwashing using hollow fibre in the filtration of produced water was significant. Using shorter intervals compared to 25 minutes with ceramic filtration of produced water and

40 minutes with spent drilling fluids, the shorter interval with hollow fibre did not improve the outcome. Though the method used in ceramic filtration of produced water to calculate resistances cannot be used to calculate resistances with hollow fibre membrane the loss to irreversible fouling is considerably high during produced water filtration.

At oil concentrations above 200 mg/L it is deduced that produced water filtration using hollow fibre membranes is not advisable. The hydrophobic nature of the PVDF membrane makes it absorb a lot of the oil and thus difficult to maintain the flux during filtration. At oil concentrations less than xxx mg/L it is seen that filtration and loss of flux is not an issue. There are also two dimensions to fouling in the hollow fibre, there is the intra membrane fouling possible in the hollow fibre strand and there is the intra-membrane fouling within the spaces of the hollow fibre strands. Backwashing would have limited effects on the intra-membrane fouling and this might be one of the reasons why its ability to reclaim the flux is limited. Maybe a combination of backwashing and backflushing would be the adequate technique for fouling mitigation in produced water filtration using hollow fibre membranes.

5.3 Membrane Chemical Cleaning

5.3.1 Introduction

The last section discussed the membrane fouling mitigation technologies aimed at prolonging the onset of flux decline or reclaiming the flux after concentration polarization or reversible fouling. These technologies are designed to address physical fouling of the membranes but are inefficient when the cause of membrane fouling is chemical in nature. Irreversible fouling as defined in this thesis is fouling that exists when the flux cannot be regained by adjustments made during membrane operation such as backwashing or membrane flushing. The cause of irreversible fouling is assumed to also be chemical in nature aside from the possibility of physical fouling which is assumed to be negligible or associated with chemical characteristics of the feed.

The chemical nature of irreversible fouling would be largely due to the interaction between the feed components and the membrane material; it is assumed that this also affects the recalcitrant physical fouling remaining on the membrane. No matter the feed being filtered, there would be a level of irreversible fouling after each filtration cycle and continued accumulation of this fouling would eventually cause permanent fouling on the membranes. This section is designed to investigate flux recovery using chemical treatment of the membrane using two chemical cleaning solutions.

The objective of this section is to investigate the efficacy of two cleaning solutions in recovering flux against irreversible fouling. Two different membrane cleaning solutions were used in our investigation, the Divos 110 alkaline detergent for UF membranes produced by JohnsonDiversey, Sharonville, Ohio and a patented aqueous surfactant composition protected by US patent 6130199 from a well bore cleaning company in Texas. The Divos 110 alkaline detergent is described by the manufacturers as a moderately foaming caustic, alkaline detergent liquid for the cleaning of chlorine stable ultrafiltration and microfiltration membranes. When using the Divos 110, Divos Add 3 a detergency booster for oil removal from all membranes is also added. The aqueous surfactant, the second cleaning agent, is described to contain an alkyl polyglycoside, ethoxylated alcohol and a caustic and an alkyl alcohol in specified concentrations to make the cleaning solution. The aqueous surfactant solution is advertised to remove hydrocarbonaceous materials and finely divided inorganic solids from well bore surfaces and other surfaces.

Two membrane “state” types were cleaned in this investigation for the ceramic membranes. Membranes as used in resistance determination and membranes as used in backwashing operations. Membrane as used in resistance determination filtered the feed without any fouling mitigation such as backwashing during the entire filtration carried out on them. The membranes were used to filter the feed for within 4 – 6 hours and the only cleaning done was clean water flushing at a higher cross flow velocity for 5 minutes. The membranes as used in fouling mitigation filtered for between 4-5 hours and they had backwashing at some interval for the entire duration of filtration.

The membranes as used in backwashing operation had lower levels of irreversible fouling compared to the membranes as used in filtration resistance determination and the difference was more significant for produced water filtration than for drilling fluids filtration. The relevance of the comparison is not fundamental but since data was collected for both cleaning processes they are presented here. The membranes as used for resistance determination would represents filtration with the intent to foul while the membranes as used in backwashing represents filtration with to minimize fouling.

The cleaning regimen for both cleaning solutions the Divos 110 and the aqueous surfactant solution was carried out according to the manufacturer's specification. For the Divos 110, two washes where needed; the alkaline wash using the Divos 110 and the acidic wash using 0.5% Nitric acid. For the alkaline wash, 1% per volume of Divos 110 is made with clean water and 0.1% per volume of Divos Add 3 is also added to the water. The alkaline solution has a yellow appearance and a pH of about 6.8. The solution is heated to 120 F and it is circulated in the membrane (recycle mode) for 40 minutes, after 40 minutes the membrane is flushed with RO water for 10 minutes, this is the end of the alkaline wash. After the clean water flush, laboratory prepared 0.5% Nitric acid is circulated in the membrane for 30 minutes and afterwards also flushed with clean water. The clean water flux of the membrane is taken before and after the whole alkaline and acid wash. Volume used is between 3-5 gallons of the solution and wash time is approximately 80 minutes.

For the aqueous surfactant solution, the recipe to make the cleaning solution is specified by the manufacturer, it involves water and four chemical additives, the solution is mixed to be homogenous and it has a slightly viscous but clear appearance. It is not heated and it is circulated at filtration temperature of about 40 C through the membrane for 40 minutes. The clean water flux is recorded before and after the circulation. The membrane clean water flux recovery is the only measure used to determine the efficacy of the cleaning solution. To determine the cleaning efficiency the initial clean water flux (J_i) was recorded before filtration, the clean water flux after filtration and flushing with distilled water (J_f) was recorded and the clean water flux after cleaning with the chemical solution was recorded (J_c). To determine the clean water flux recovery it was calculated as

$$Flux\ recovery = \frac{J_i - J_f}{J_c - J_f} \tag{5.1}$$

Usually after flushing with distilled water i.e. cleaning at high cross flow velocity the membranes are usually retuned to within 40 -70 percent of the original clean water flux depending on the condition of filtration and the amount of flux lost. For example filtration at higher pressures showed high flux loss and lower flux recovery after flushing, the results shown here are for situations where the clean water flux recovery was less than 60% after flushing.

5.3.2 Flux Recovery in Ceramic Filtration of Spent Drilling Fluids

After ceramic filtration of spent drilling fluids the clean water flux, flux after RO flush and flux after cleaning are presented in table 5.1 with the filtration condition under which the feed was filtered.

Table 5.1 Chemical cleaning of ceramic membrane after filtration of spent drilling fluids

Cleaning Agent	Initial water flux (J_i) GFD	Flux after flush (J_f) GFD	Flux after clean (J_c) GFD	Filtration condition
Divos 110	116.57	32.30	110.86	High transmembrane pressure (20 psi), 4 hours filtration, no backwash
Divos 110	115.32	93.69	114.49	Normal transmembrane pressure (12 psi), 4 hours filtration, backwashing
Aqueous Surfactant Solution	118.41	40.33	110.72	High transmembrane pressure (20 psi), 4 hours filtration, no backwash
Aqueous Surfactant Solution	119.17	91.45	117.00	Normal transmembrane pressure (12 psi), 4 hours filtration, backwashing

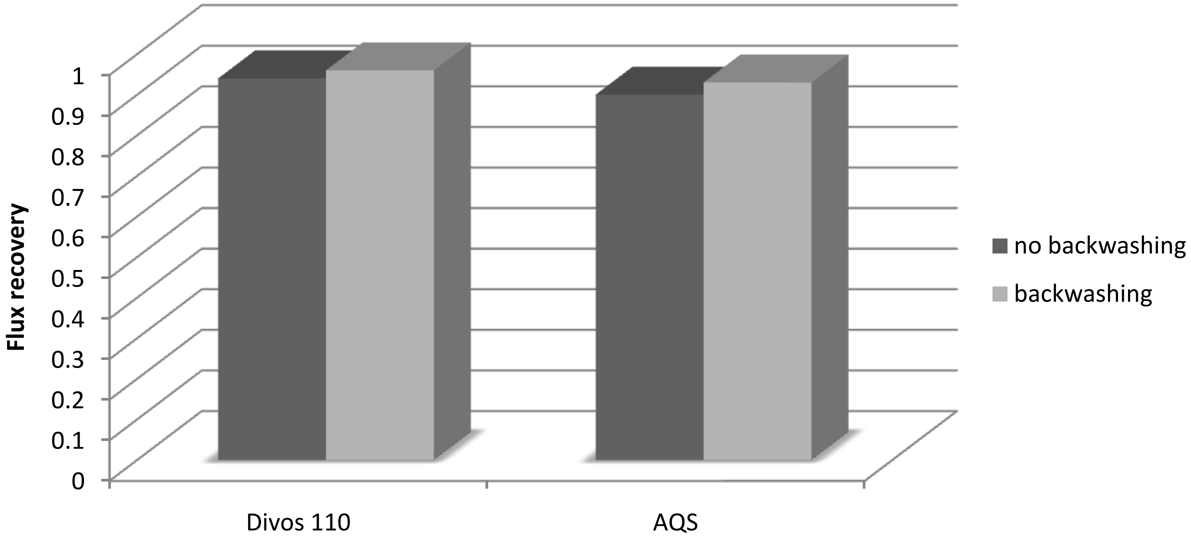


Fig. 5. 4 Flux recovery of ceramic membrane cleaning after filtration of spent drilling fluids. Cleaning agent include Divos 110 and aqueous surfactant solution (AQS).

Figure 5.4 shows the clean water flux recovery using two cleaning solutions Divos 110 (with Divos Add 3) and an aqueous surfactant solution (AQS) for ceramic membrane filtering of spent drilling fluid with and without backwashing. Table 5.1 explains the filtration condition at which the experiments were carried out. In the filtration without backwashing the condition was under high transmembrane pressure of 20 psi a filtration condition certain to induce fouling; the flux before chemical cleaning and after RO flushing is 30% of the clean water flux. 70% of the flux at this condition was not recovered with RO water flux but after cleaning with Divos 110, 94% of the clean water flux was recovered. In the filtration where backwashing was applied to the membrane periodically, the flux before chemical cleaning and after RO flushing is 80% of the clean water flux, after treatment with Divos 110 96% of the flux was recovered.

For the cleaning efficiency using the aqueous surfactant solution, when there is no backwashing and under high transmembrane filtering condition the flux recovered using RO flushing is 34% of the clean water flux i.e. 66% of the clean water flux was unrecoverable. After cleaning with the aqueous solution 90% of the clean water flux was recovered. For the condition with backwashing, after RO cleaning, 78% of the clean water flux was recovered with the RO flushing, after cleaning with the aqueous surfactant solution the clean water flux recovery was 93% of the initial clean water flux. Filtration at the set arbitrary values used to generate flux decline curves (chapter III) for spent drilling fluids would usually after RO flushing recover 60-80% of the clean water flux similar to what obtains during backwashing, but at high pressures the recovery is lower and thus were better suited to determine cleaning efficiencies.

5.3.3 Flux Recovery in Ceramic Filtration of Produced Water

After ceramic filtration of produced water the clean water flux, flux after RO flush and flux after cleaning are presented in table 5.2 with the filtration condition under which the feed was filtered.

Table 5. 2 Chemical cleaning of ceramic membrane after filtration of produced water

Cleaning Agent	Initial water flux (J_i) GFD	Flux after flush (J_f) GFD	Flux after clean (J_c) GFD	Filtration condition
Divos 110	113.14	74.85	109.53	High transmembrane pressure (20 psi), 4 hours filtration, no backwash
Divos 110	117.56	105.14	116.69	Normal transmembrane pressure (12 psi), 4 hours filtration, backwashing
Aqueous Surfactant Solution	114.38	70.19	108.92	High transmembrane pressure (20 psi), 4 hours filtration, no backwash
Aqueous Surfactant Solution	114.31	94.30	112.18	Normal transmembrane pressure (12 psi), 4 hours filtration, backwashing

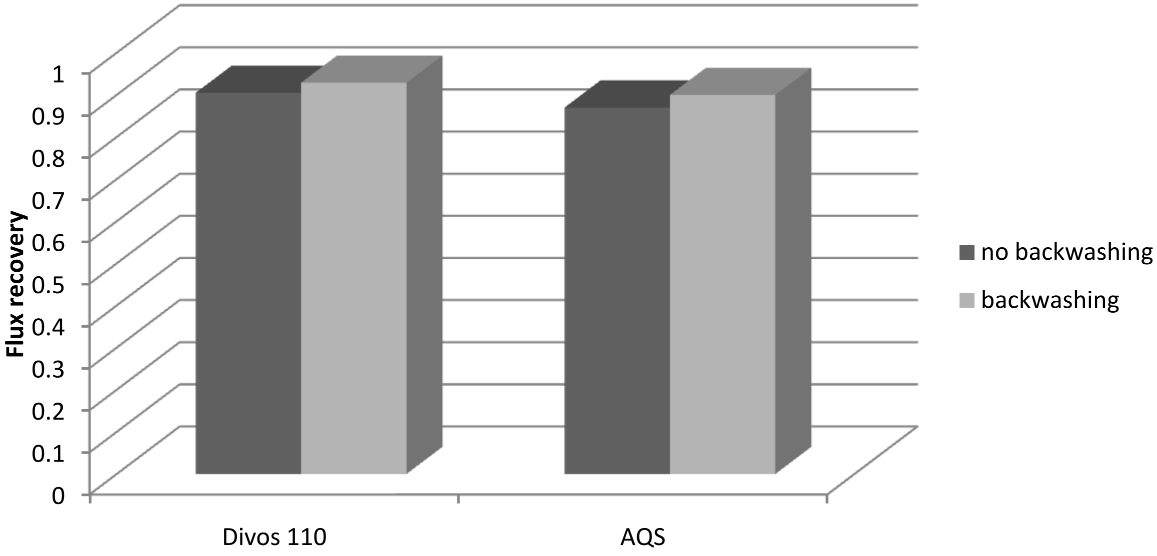


Fig. 5. 5 Flux recovery of ceramic membrane cleaning after filtration of produced water. Cleaning agent include Divos 110 and aqueous surfactant solution (AQS).

Figure 5.5 shows the clean water flux recovery using two cleaning solutions Divos 110 (with Divos Add 3) and an aqueous surfactant solution (AQS) for ceramic membrane filtering of produced water with and without backwashing. Table 5.2 explains the filtration condition at which the experiments were carried out. In the filtration without backwashing the condition was under high transmembrane pressure of 20 psi a filtration condition certain to induce fouling; the flux before chemical cleaning and after RO flushing is 66% of the clean water flux. 34% of the flux at this condition was not recovered with RO water flux but after cleaning with Divos 110, 90.5% of the clean water flux was recovered. In the filtration where backwashing was applied to the membrane periodically, the flux before chemical cleaning and after RO flushing is 90% of the clean water flux, after treatment with Divos 110 93% of the flux was recovered.

For the cleaning efficiency using the aqueous surfactant solution, when there is no backwashing and under high transmembrane filtering condition the flux recovered using RO flushing is 62% of the clean water flux i.e. 38% of the clean water flux was unrecoverable. After cleaning with the aqueous solution 87% of the clean water flux was recovered. For the condition with backwashing, after RO cleaning, 82% of the clean water flux was recovered with the RO flushing, after cleaning with the aqueous surfactant solution the clean water flux recovery was 90% of the initial clean water flux. Filtration at the set arbitrary values used to generate flux decline curves (chapter III) for spent drilling fluids would usually after RO flushing recover 60-80% of the clean water flux similar to what obtains during backwashing, but at high pressures the recovery is lower and thus were better suited to determine cleaning efficiencies.

5.3.4 Flux Recovery in the Hollow Fibre Filtration of Produced Water

After the hollow fibre filtration of produced water the clean water flux, flux after RO flush and flux after cleaning are presented in table 5.3 with the filtration condition under which the feed was filtered. The hollow fibre membrane resistance calculation was not carried out (Chapter IV); the conditions of filtration have only the conditions where the flux decline experiments for 6 hours were carried out. The oil concentration in all cases was less than 300 ppm.

Table 5.3 Chemical cleaning of hollow fibre membrane after filtration of produced water

Cleaning Agent	Initial water flux (J_i) GFD	Flux after flush (J_f) GFD	Flux after clean (J_c) GFD	Filtration condition
Divos 110	986	288	754	Transmembrane pressure (12 psi), 4 hours filtration, no backwash
Aqueous Surfactant Solution	1016	219	918	Transmembrane pressure (12 psi), 4 hours filtration, no backwash

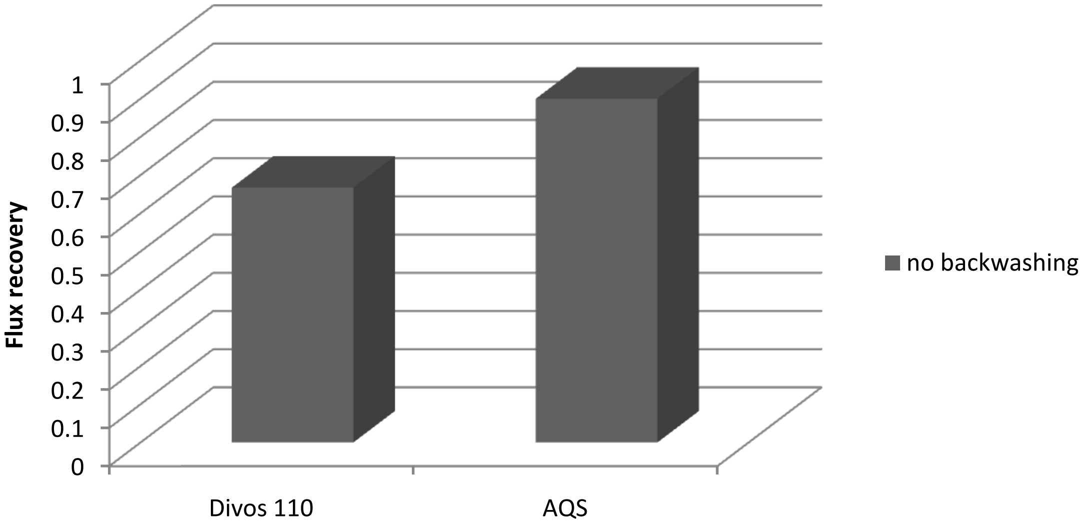


Fig. 5. 6 Flux recovery of hollow fibre membrane cleaning after filtration of produced water. Cleaning agent include Divos 110 and aqueous surfactant solution (AQS).

Figure 5.6 shows the clean water flux recovery using two cleaning solutions Divos 110 (with Divos Add 3) and an aqueous surfactant solution (AQS) for hollow fibre membrane filtering of produced water without backwashing. Table 5.3 explains the filtration condition at which the experiments were carried out. In the filtration without backwashing the condition was under transmembrane pressure of 12 psi a filtration condition certain to induce fouling; the flux before chemical cleaning and after RO flushing is 30% of the clean water flux. 70% of the flux at this condition was not recovered with RO water flux but after cleaning with Divos 110, 76% of the clean water flux was recovered.

For the cleaning efficiency using the aqueous surfactant solution, when there was no backwashing and under transmembrane pressure of 12 psi, the flux recovered after RO flushing was 21% of the clean water flux i.e. 79% of the clean water flux was unrecoverable. After cleaning with the aqueous solution 90% of the clean water flux was recovered. The polymeric membranes when not in use were stored in a cleaning solution because the membrane had to be wet, when left in the sanitizing solution overnight the membrane flux returned to the initial clean water flux at all times.

5.4 Summary

The cleaning solution Divos 110 recovered more of the clean water flux for ceramic membranes above the aqueous surfactant solution and in cleaning the polymeric PVDF hollow fibre membrane the aqueous surfactant solution recovered more of the clean water flux. The Divos 110 cleaning solution has a more robust cleaning cycle as the alkaline cleaning cycle is followed by an acidic cycle, the alkaline cleaning agent are effective in breaking the bonds between the membrane surface and the fouling layer [40,72]. While acids are effective in getting rid of inorganic salts[40], insoluble salts and metal oxides [73 and Nitric acid is a strong oxidant causing nitrification of organic compounds [48]. The aqueous surfactant solution contain hydrophilic and hydrophobic functional groups that enhance the wettability and rinsability, increase contact area between the foulants and the active agents hereby dislodging the foulants easily.

The clean water flux recovery was higher in all cases for the membrane state type where there was backwashing. As explained the backwashing reduced the proportion of irreversible fouling relative to a membrane that filtration occurred without backwashing, intuitively the cleaning process is less tasked in with backwashed membranes as the fouling start point is lower. Recovery was within 90-96% of the initial clean water flux in the ceramic filtration of both feed types using the Divos 110, while it was between 87-93% of the clean water flux recovery when the aqueous surfactant solution was used for both feed using ceramic filtration. More clean water flux recover was achieved in the filtration of drilling fluids relative to produced water; this underscores the variability and complexity in produced waters.

For the cleaning of the polymeric PVDF hollow fibre material the aqueous surfactant solution recovered more of the clean water flux compared to the ceramic membrane, it is not fully understood the reasons for this but surfactant action gave a cleaner membrane compared to the alkaline and acidic wash of the Divos 110 cleaning cycle. Flux recovery of using the aqueous surfactant solution was 91% of the original clean water flux compared to about 70% recovery of the clean water flux when using the Divos 110. Polymeric material membranes cannot be left dry they need to be soaked in some cleaning solvent to keep the membranes wet. After use the membranes are always soaked in ultrasil xxx to sanitize the membrane, when soaked overnight with the sanitizer the membrane returns to its original clean water flux despite the cleaning solution used in most cases.

In comparing the two cleaning chemicals no optimization was done to improve the cleaning regimen. Time, temperature, water quality used, fluid mechanics and pH [48, 49]are factors capable of affecting the cleaning solution efficiency. Though the Divos 110 cleaning agent shows a higher efficiency at cleaning than the aqueous surfactant solution, it has to be heated to 120 F for the alkaline wash and contains two wash cycles and two flushes thereby a longer cleaning regimen. All these factors apart from cleaning efficiency are necessary in selecting a cleaning agent for both pilot and industrial purposes.

CHAPTER VI

CONCLUSION AND RECOMMENDATIONS

6.1 Introduction

Increasing energy demand is spurring exploitation of unconventional resources and conventional resources while increasing subsurface reach would increase the foot print of exploration and production activities, significantly changing the dynamics of environmental impact. Stricter environmental protection demands, fresh water sourcing and waste volume management shall increasingly narrow the availability of reservoirs that can be exploited by the oil and gas industry. Waste volumes generated are increasingly bearing on alternative waste treatments that are environmentally friendly forcing less re-use and recycle of waste streams that can be used for non-consumption purposes. The positioning of exploration and production waste management as a central factor in the decision to exploit oil and gas resources shall amplify with time if the current trend continues.

Water based exploration and production wastes are a substantial portion of oil and gas waste produced, they are also the least recycled or re-used as disposal permits or large scale treatment systems such as injection reduce the incentive for treatment. This class of wastes is expected to increase as water cut increases, subsurface reach increases, unconventional reservoirs exploitation increase, use of environmentally friendly drilling fluids increase and exploration and production activities increase. The need for technologies aimed at making these water based wastes amenable to re-use or pre-treating these wastes so that they can be subjected to other treatment systems such as desalination is increasing daily. Steps at waste management to increase economical re-use of these wastes in fields would go a long way at cost reduction of waste disposal.

Irrespective of the treatment methods aimed at recycle or re-use of these water based wastes a step by step treatment objective should be laid out for the treatment of the wastes after feed characterization. In this thesis solids concentration removal was the treatment objective in the treatment of spent drilling wastes to achieve solids concentration or in oil-field terms dewatering. In the treatment of produced water the treatment objective was mechanical pre-treatment using microfiltration or ultrafiltration in the removal of oil concentration and suspended solids for desalination of produced water. These objectives determined the type of membranes used, the operational objectives set, the fouling mitigation and cleaning procedures adopted and the characterization of the wastes needed.

6.1.2 Spent Drilling Fluids Filtration Using Ceramic Membranes

Membrane filtration of spent drilling fluids using ceramic ultrafiltration and microfiltration membranes was successful, there was between 95-99% solids rejection after filtration. The permeate was mostly solids free and had low concentrations of suspended solids. The dissolved constituent of the feed were unaffected by filtration at the pore sizes used. Flux values were moderate and fouling mitigation and chemical membrane cleaning were effective in reclaiming the clean water flux. Permeate quality differences existed using different pore sizes but were not very significant, the larger the pore size the larger the flux and fortunately within 0.005 to 0.2 microns the fouling pattern was significant. In order words for a pilot scale study using the larger pore size 0.2 micron would be beneficial as it gives a higher flux and the membrane fouling pattern is not significantly greater than the fouling pattern at smaller pore sizes.

High cross flow velocities created the largest gain in permeate volume compared to other operational parameters varied. Operating at high temperature was also beneficial to maintaining and increasing membrane flux, as much as possible using ceramic membranes at high temperatures would be beneficial for higher fluxes and fouling mitigation. The feed solids concentration was the most important parameter in the filtration of the spent drilling fluids, solids above 10.20% solids volume (~30,000 mg/L) gave very low fluxes, solids volume less than 8.8% solids (`19,000 mg/L) gave better fluxes. The solids concentration and distribution would is beneficial to fouling mitigation at the appropriate filtration conditions. Possible pre-treatment would involve the reduction of solids to filterable levels while maintaining a diverse solids distribution. The effect of the dissolved constituents on filtration was not individually characterized and would need to be determined with respect to membrane flux and cleaning for similar feed types.

6.1.3 Produced Water Filtration Using Ceramic Membranes

Membrane filtration of produced water using ceramic ultrafiltration and microfiltration membranes was successful in the removal of oil and suspended solids, there was between 95-99% oil rejection and 99% turbidity after filtration. The permeate was mostly oil free and had low concentrations of suspended solids. The permeate exceeded the 5 NTU needed to optimizes desalination, with an average of 1.16 NTU. The dissolved constituent of the feed were unaffected by filtration at the pore sizes used. Flux values were moderate and fouling mitigation and chemical membrane cleaning were effective in reclaiming the clean water flux. Permeate quality differences existed using different pore sizes but were not very significant, fouling at larger pore sizes was slightly higher than at lower pore sizes. Oil concentration not solids concentration plays the significant role in the flux decline during filtration using ceramic membranes.

High temperatures created the largest gain in permeate volume compared to other operational parameters varied. Operating at high cross flow velocity was also beneficial to increased membrane flux but was qualified in prolonging the onset of fouling. As much as possible high temperatures would be beneficial for higher fluxes and to a lesser extent in fouling mitigation of produced water filtration. The feed oil concentration was the most important parameter in the filtration of the produced water, oil concentration above 1,200 ppm gave the least optimized flux but oil concentration below 500 ppm gave higher fluxes. Pre-treatment to the feed entering the ceramic membrane should be for the removal of large particle size and to reduce oil concentration to optimize filtration. Dissolved solids characterization except for some divalent ions was not carried out, for the concentrations range of divalent ions specified, the effect on filtration was minimal.

6.1.4 Produced Water Filtration Using Hollow Fibre Membranes

Membrane filtration of produced water using hollow fibre microfiltration membranes was successful in the removal of oil and suspended solids, there was between 95-99% oil rejection and 99% turbidity after filtration. The permeate was mostly oil free and had low concentrations of suspended solids. The permeate exceeded the 5 NTU needed to optimizes desalination, having an average of 1.8 NTU. The dissolved constituent of the feed were unaffected by filtration at the pore sizes used. Flux values were high at low oil concentrations, fouling mitigation and chemical membrane cleaning would only be effective in reclaiming the clean water flux at low feed oil concentrations. Feed oil concentration played the major role in the flux decline as oil concentrations higher than 300 ppm caused significant flux decline.

High temperatures created the largest gain in permeate volume compared to other operational parameters varied. Operating at high cross flow velocity and temperature within the manufactures parameter was not beneficial to increased membrane flux and in prolonging the onset of fouling. As much as possible high temperatures would be beneficial for higher fluxes within the membrane specified temperature range and to a lesser extent in fouling mitigation of produced water filtration. The feed oil concentration was the most important parameter in the filtration of the produced water, oil concentration above 500 ppm gave the least optimized flux but oil concentration below 300 ppm gave high fluxes. Pre-treatment to the feed entering the ceramic membrane should be for the reduction in oil concentration and removal of large particle (greater than 10 micron) to optimize produced water filtration. Dissolved solids characterization except for some divalent ions was not carried out, for the concentration range of divalent ions specified, filtration was unaffected.

6.1.5 Membrane Resistance Cleaning and Fouling Mitigation Technologies.

High pressures accelerated the fouling of the membrane during filtration of all types of feed and membrane types. High cross flow velocities were beneficial in prolonging the onset of fouling, in high solids concentration feed like spent drilling fluids, high cross flow velocities were effective in maintaining flux. Temperature effect on resistances showed no clear pattern. The dominant fouling mechanism in the filtration of solids concentration is believed to be cake layer formation though pore plugging plays a role. In the filtration of produced water cake layer formation is also believed to be prominent though pore plugging is apparent, the losses after backwashing could be attributed to blocked pores. From the results of backwashing, the cake layer adhesion in produced water filtration is loose as high cross flow velocity flushing shows a high recovery of the flux. Hollow fibre membrane filtration fouling was not determined in this experiment, inter and intra fibre fouling create an added layer of complexity in determining the fouling mechanism using hollow fibre membranes.

Fouling mitigation using backwashing was very effective in the filtration of produced water using ceramic membranes, flux recovery was high and the recovery with time was fairly constant within the experiment time frame. Backwashing was effective in flux recovery in the spent drilling fluids filtration using ceramic membranes, the recovery rate reduced with time and at one point there shall be a saturation of the benefits of backwashing. Absorption of the oil by the hydrophobic PVDF membrane of the hollow fibre membrane made backwashing of little value especially at oil concentrations above 300 ppm. At low oil concentrations i.e. below 300 ppm, backwashing or fouling mitigation had very limited use in the produced water filtration using hollow fibre membranes.

Flux recovery using the two chemical cleaning agents were effective in the recovery of flux with the Divos 110 alkaline cleaning agent from Johnson diversey showing more recovery in the cleaning of ceramic membranes. The aqueous surfactant solution was more effective in the cleaning of the PVDF hollow fibre membrane. The aqueous surfactant membrane could be a better choice as there is no need to heat though it is less efficacious in ceramic membrane cleaning.

6.2 Recommendations

To apply practically membranes to a particular waste streams these recommendations are deemed useful to make that determination.

6.2.1 Waste Characterization

Oil field wastes show significant variability and this poses one of the biggest challenges to membrane filtration. Feed variability hinders the ability to stabilize flux values, reduces the comprehension on foulants subjecting the membranes to fouling. A simple characterization can be done based on the figure 6.1.

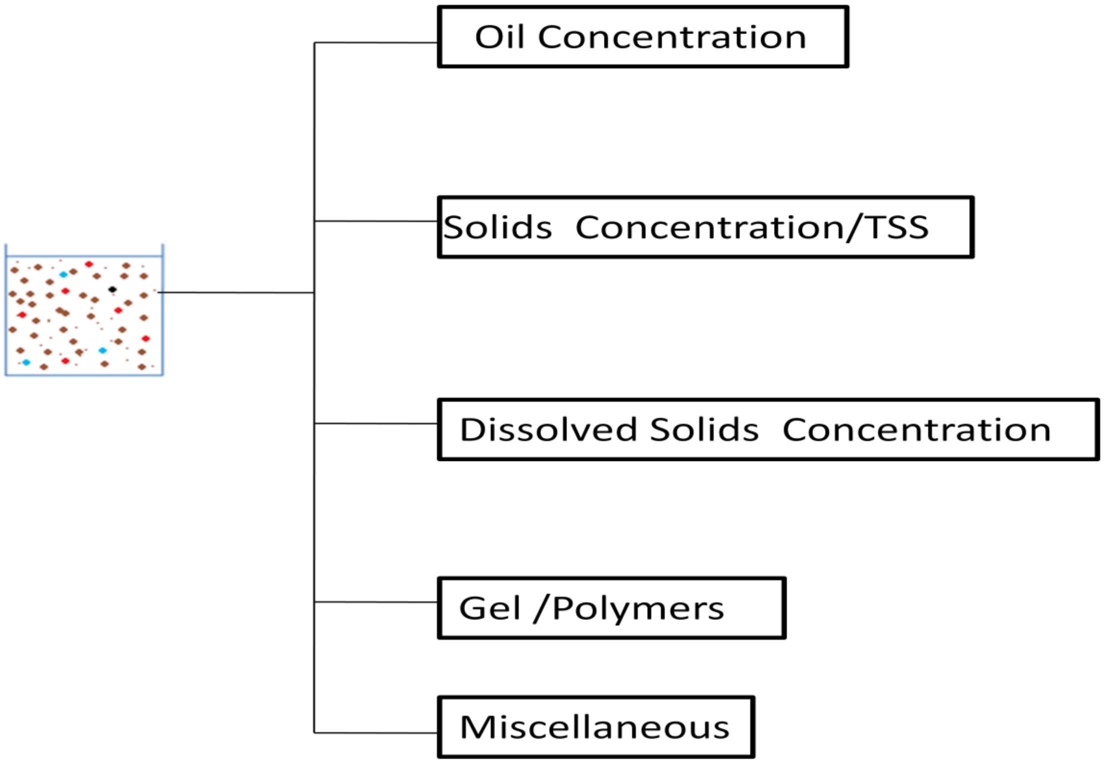


Fig. 6. 1 Waste characterization of E&P wastes to determine membrane filtration compatibility.

A simple waste characterization in the consideration of water based E&P wastes for membrane filtration would be a characterization based on oil concentration, suspended solids concentration, dissolved solids concentration, gel or polymers and miscellaneous categorization. Depending on the intention for filtration, the characterization of the feed allows for better determination of the membrane type most suitable and the membrane system most appropriate.

As much as possible gels and polymers should be removed before filtration through membranes, depending on their constituents they might accelerate fouling, chemically react with the membranes, increase viscosity of the feed thereby reducing the flux. Chemical pre-treatment for the removal of gels and polymers might be essential upstream of membrane filtration. Categorization based on miscellaneous characteristics would be essentially geared towards properties of the feed that would affect membranes such as the presence of corrosive properties, solvents, temperature of the feed, pH of the feed and pertinent information that could be detrimental to membrane functioning. These allow for appropriate pre-treatment before membrane filtration.

High oil concentration > 1200 ppm can go through pre-treatment before ceramic membrane filtration to bring down the oil concentration using treatments such as adsorbents to lower the oil concentration remarkably. Also higher high oil concentration can be accommodated if efficient fouling mitigation and cleaning methodologies are employed in the operation of the membrane, this would be an operational decision. Low oil concentrations (<300 ppm) with low solids concentration (<2000 mg/L) would be great feed for hollow fibre membranes as the flux rate is superior at these conditions to ceramic membranes. Two stage treatments can also be encouraged where ceramic membranes treat feed with high oil concentrations and the hollow fibre are used as a cleaning step either for further treatment or just for re-use.

Ceramic membranes are effective in high solids feed up to 18,000 mg/L as they showed rejection rates up to 99%, low solids (less than <2000 mg/L) would be suitable for both membranes types with the hollow fibre more appropriate due to higher fluxes. Depending on the desired flux rate, pre-treatment of the waste to reduce the total suspended solids could be carried out; solids concentrations lower than the upper limit used here would guarantee better flux in the absence of chemical foulants. Depending on the intended flux high solids in ceramic membranes can be handled if good fouling mitigation techniques are applied. Issues with high solids feed filtration would be abrasion on the membrane surface or the erosion on the entrance of the membrane; these should be factored in determining the life cycle of the membrane under constant use. When there is a high rise in the clean water flux relative to prior reading or quick fouling of the membranes there is possibility of abrasion by solids of the membrane surface, this was not noticed in our testing of the ceramic membranes.

The major effect of the dissolved solids in the ultrafiltration and microfiltration of feeds centers around their effect on fouling. The effects of dissolved solids were not studied in this study due to the variation in their concentrations in the feed sample i.e. the presence of various dissolved solids from sample to sample and the varied concentrations. Specified ranges of dissolved solids were chosen as a criterion to give some form uniformity to the feed. In filtration operations, the effect of dissolved solids interaction with membrane material would be very important, the more inert the material is the lesser the propensity of fouling and the more reactive the membrane material is the greater the propensity of fouling.

Feed variation control would be the most important operational parameter in the filtration of water based E&P wastes. Better characterization of the wastes would allow for determination of upstream treatments needed before microfiltration or ultrafiltration, this would also allow for effective membrane filtration and cleaning strategy. Due to practical limitations in maintaining feed uniformity from diverse oil and gas operations, ranges could be specified as exemplified in this study, above those ranges pre-treatment could be applied to bring the value within range.

6.3 Limitations

The laboratory membrane system used in this study was the most simplistic membrane filtration outlay, it was not optimized for performance and thus the flux rates would be lower than what would be obtained using optimized membrane systems. Feed characterization of produced water was not extensive and thus the roles of completing influences such as dissolved solids was not isolated for contribution to fouling of both feed types. Studies of this nature are designed as proof of concept to determine membrane suitability to the chosen waste types; this does not diminish the need for pilot testing to recognize issues closely associated with scaling. The results presented are best interpreted within the determination of membrane material and module suitability for filtration of the feed and the efficacy of fouling mitigation and cleaning methodologies.

6.4 Recommendations

This study shows the potential of membranes as a waste management tool in the re-use and recycle of water based E&P wastes. Fouling and low fluxes remain the greatest challenges to membrane adoption, investigation into feed characterization and the effect of various components of the feed on membrane fouling would be beneficial. For practical systems investigation into pre-treatments that could help reduce the effect of feed concentration on membrane filtration would yield the highest dividend to water based E&P

wastes filtration. Fouling mitigation technologies and environmentally degradable cleaning solutions would also be another area of interest in the application of membranes to this class of waste. Finally the translation of this laboratory results to pilot scale would enhance a better understanding of issues creating an iterative process that would feed more knowledge into this quest.

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