DEASHING OF COAL LIQUIDS WITH CERAMIC MEMBRANE MICROFILTRATION AND DIAFILTRATION

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Introduction

Removal of mineral matter from liquid hydrocarbons derived from the direct liquefaction of coal is required for product acceptability. Current methods include critical solvent deashing (Rose® process from Kerr-McGee) and filtration (U.S. Filter leaf filter as used by British Coal). These methods produce ash reject streams containing up to 15% of the liquid hydrocarbon product.

Consequently, CeraMem proposed the use of low cost, ceramic crossflow membranes for the filtration of coal liquids bottoms to remove mineral matter and subsequent diafiltration (analogous to cake washing in dead-ended filtration) for the removal of coal liquid from the solids stream. The use of these ceramic crossflow membranes overcomes the limitations of traditional polymeric crossflow membranes by having the ability to operate at elevated temperature and to withstand prolonged exposure to hydrocarbon and solvent media. In addition, CeraMem's membrane filters are significantly less expensive than competitive ceramic membranes due to their unique construction. With these ceramic membrane filters, it may be possible to reduce the product losses associated with traditional deashing processes at an economically attractive cost.

Membrane Background

General Description of Crossflow Membrane Processes

The process for removal of solids from coal derived liquids in this program is crossflow microfiltration (MF). This is a pressure driven membrane process in which particulate and colloidal materials are removed from a feed stream (See Figure 1). In microfiltration, the feed stream is pumped over the membrane surface with a transmembrane pressure differential in the range of 20 to 100 psi. The crossflow velocity is generally 100 to 10,000 times the "perpendicular" velocity or filtration velocity. Retained matter is removed from the system as a fluid concentrate. The surface shear at the membrane surface controls the build-up of a filter cake (or membrane foulant layer) so that, in principle, a steady sate filtration rate is attained. The process is to be contrasted with dead-ended filtration in which no crossflow is present and a filter cake builds continuously as filtrate is removed.

MF is generally employed for removal of submicron particulate and colloidal matter which would rapidly blind surface filters. Also, MF replaces diatomaceous earth precoat filters because of greater product recovery and the elimination of waste disposal of a voluminous spent precoat cake.

MF can be used in a diafiltration process to increase the recovery of liquid or soluble products from a particulate containing stream. In diafiltration, a solvent is added to the fluid concentrate to dilute the solids so that the fluid can be refiltered to remove additional product in the filtrate along with some of the added solvent. Several cycles of this process can be used such that essentially all the product in the feed stream is removed and the concentrate consists of solids and solvent. Additional processing of the permeate and/or concentrate may be necessary in order to remove the solvent depending on the application.

Description of CeraMem's Ceramic Crossflow Membrane Technology

CeraMem is one of several commercial suppliers of liquid crossflow ceramic membrane modules which utilize a porous ceramic monolith as a membrane support. However, CeraMem is unique in its approach, described below, in utilizing a very high membrane surface area support structure in each modular element.

Ceramic Monoliths as Membrane Supports. CeraMem's technical approach to construction of ceramic membrane modules is based on the use of porous honeycomb ceramic monoliths as membrane supports. These high surface area, low cost materials have been developed for and are widely used as catalyst supports for automotive catalytic converters. The most commonly available material is cordierite. Cell (i.e., feed passageway) "areal densities" in the honeycomb structure range from 9 to 1400 cells per square inch of monolith frontal area (cpsi), and can have cell geometries of round, square, or triangular. The porosity of the materials can range from about 30% to 50% with mean pore diameters of 3 μm to 35 μm. The monoliths themselves can be extruded in various cross sections such as rounds, ovals, or squares. Cross sections up to 13" and lengths up to 36" are extruded on a commercial scale by Corning, Inc.

Membrane Application to the Ceramic Support. CeraMem forms microfiltration and ultrafiltration membranes on the monolith by slip casting porous coatings of ceramic particles on the cell wall surfaces of the passageways, followed by drying, and then sintering to bond the particles to each other and the honeycomb support. Most membranes have more than one coating layer, constituting a multilayer, asymmetric ceramic membrane. The initial layers are relatively thick (75-100 μm) and consist of large particles to cover the pores of the support material. Subsequent layers are thinner to minimize flow resistance and consist of finer particles to form finer pore sizes. A schematic diagram of a multilayer membrane is shown in Figure 2.

Mode of Use As Membrane Supports/Housing and Seal Design Concept. Each monolith has hundreds to thousands of parallel passageways that run from one face to the opposite end face (Figure 3). During processing, the feed stream to be treated is introduced under pressure at one end of the module, flows through the passageways over the membrane, and is withdrawn at the downstream end of the module. Material which passes through the membrane (permeate) flows into the cell walls of the monolith. The combined permeate from all the passageways flows toward the periphery of the monolith support, and is removed through an integral, pressure-containing "skin" at the exterior of the monolith.

There is a technical limitation to use of monolith supports as described above. Due to the long and tortuous path through which the permeate must flow to get to the outside pressure containing skin, there can be a large pressure drop for permeate flow. Depending on membrane resistance and process conditions, the only passageways from which permeate can be effectively removed are often those in an annular ring adjacent to the monolith skin. This limitation generally restricts the diameter of monoliths than can be used to approximately one inch.

CeraMem has developed mechanical modifications to monoliths to overcome this limitation, and one version is used commercially for membrane modules of approximately six inches in diameter. These mechanical modifications create permeate conduits within the monolith which conduct permeate from the interior of the monolith to an external permeate collection zone. Figure 4 depicts one form of these mechanical modifications. In this case, slots are cut into one end (or both) of the monolith, and the ends of these slots are sealed. At the opposite end of the monolith, the ends of the cells opening into the slots are sealed in a like manner. Many sealants can be used, but the preferred materials are similar to that from which the monolith is made. After sealing the slots at both ends of the monolith, the monolith is coated with membrane. During operation, feed is pumped through the module, and permeate flows through the membrane into the monolith cell walls. The permeate from any cell in the monolith flows no more than a few cell layers before it arrives at a low pressure permeate conduit. When the conduit is reached, the permeate flow turns toward the end of the monolith containing the slots. Upon reaching the slots, the permeate flow turns 90° and flows into a permeate collection zone.

This approach to removing permeate from the inside of a large diameter monolith results in high surface area modules with very high membrane packing densities. As a result, several advantages are derived from this unique membrane construction. First, since most of the cost of manufacturing ceramic membranes is labor, the cost of producing high surface area membrane elements is relatively low allowing CeraMem to sell membranes at much lower prices per square foot than other ceramic membranes and at prices competitive to polymeric membranes in some cases. Also, with the high surface area filter elements fewer elements are needed in any one system thereby minimizing the amount of associated hardware including housing and seals.

At present, the conduit configuration described above has been commercialized for crossflow liquid applications, using elastomeric boot seals in stainless steel housings, at temperatures up to 200°C. This design, however, is not readily amenable to sealing at higher temperatures due to the temperature limitation on the elastomer boot seal. CeraMem has developed high temperature membrane modules for use in petroleum-based feed stream processing at temperatures up to 350°C on a developmental basis and believes that commercial, full size filter elements with housings and seals capable of operating at higher temperatures are possible.

Proposed Technical Approach

The approach proposed for this program to deash the coal liquid bottoms entails two steps. The first step is ash concentration with crossflow MF. Residual oil, containing ash, is pumped through a ceramic membrane system operating with a transmembrane pressure of about 20-80 psi. If the feed material is generated at ambient pressure, the filtrate will be recovered at ambient pressure. If the feed is pressurized to retain volatiles, then both the concentrate and the filtrate from the membrane unit will be pressurized. The system pump provides the required crossflow velocity through the membrane elements. This concentration process produces two product streams. The filtrate, free of suspended particulates, may be further processed through the liquefaction reactors to increase product yield. The second stream is the solids containing concentrate. The suspended particulates level in the concentrate can be expected to range from about 20 to 30%. After concentrating the bottoms to this solids level, 55-76% of the liquid fraction can be recovered as filtrate if the starting mixture contains 10% solids. Additional processing of the concentrate is necessary in order to extract most of the remaining residual oil.

To increase overall oil recovery, the concentrate can be treated by diafiltration. In this process, shown schematically in Figure 5, a volatile solvent (e.g., a distillate product generated within the coal liquefaction process) would be added to the concentrate and the diluted concentrate would be further processed by crossflow MF.

Diafiltration serves to displace the resid from the concentrate with solvent. Therefore, the final concentrate from the diafiltration section consists primarily of suspended particulates and solvent. While diafiltration could be used to recover essentially all of the resid from the ash-reject stream, there will be an economic optimum for the degree of diafiltration actually employed. The diafiltration filtrate would be flashed or distilled to recover solvent for recycle. The diafiltration concentrate would be dried to recover solvent for recycle.

Project Technical Objectives

This program is directed towards development of an improved process for de-ashing and recovery of coal-derived residual oil: the use of ceramic membranes for high-temperature microfiltration and diafiltration. Using laboratory scale ceramic membrane modules, samples of a coal-derived residual oil containing ash will be processed by crossflow microfiltration, followed by solvent addition and refiltration (diafiltration). Recovery of de-ashed residual oil will be demonstrated. Data from this program will be used to develop preliminary estimates for production system capital and operating costs that will be used to assess economic feasibility.

A first objective of this program is to demonstrate technical feasibility of crossflow microfiltration (MF) for removal of mineral matter from a coal derived residual oil. A second objective is to demonstrate technical feasibility of diafiltration of MF concentrate using a hydrocarbon solvent.

Experimental Materials and Procedures

Two types of ceramic membranes were tested in coal liquids filtration. These lab scale membrane modules were approximately 12 inches long and 1 inch in diameter and had 1.5 ft^2 of membrane area. The passageways were square and approximately 0.07 inches on a side. The two membranes tested had separation layers consisting of 0.05 μm diameter pore size titania and 0.01 μm diameter pore size silica. Ceramic end rings were bonded onto each end of the module so that it could be sealed into stainless steel housings. The seal between the housing and module was a graphite packing seal used successfully in previous hydrocarbon testing.

The coal liquid and diluent used in these tests were obtained from Hydrocarbon Research, Inc. in Princeton, NJ. The coal liquid was a reactor liquid flash vessel bottoms (O-43) from a recent HRI liquefaction run (Run Number 260-004-49-T). The diluent was petroleum based, hydrotreated start-up oil (HRI Number L-809).

The process tests were performed at Imperial Oil, Ltd. in Sarnia, Ontario Canada. Imperial Oil had a high temperature crossflow test system designed for liquid hydrocarbon testing. The test system was capable of heating feeds to temperatures of about 300°C, feed stream crossflow of up to 6 gpm, and membrane inlet pressures of up to about 100 psig. The system could process the liquids in both recycle mode and batch concentration mode. In recycle mode, the permeate was recycled back to the feed tank resulting in no change in solids concentration in the feed stream. In the batch concentration mode, the permeate was diverted to an alternate vessel resulting in an increase in solids in the feed material.

Two general sets of tests were conducted on one batch of coal liquid. The flash drum bottoms were diluted from approximately 15% total suspended solids to about 10% solids. Solids concentrations were determined by a THF insolubles test according to a procedure obtained from Consol, Inc. First, filtration tests at constant solids concentration were performed to determine the effects of membrane type, temperature, pressure, and crossflow velocity. Based on the results of these initial tests, the membrane type and process conditions for the batch concentration of the coal liquid to about 20% solids was determined. After this initial batch concentration was performed on the diluted flash drum bottoms, four additional dilutions and concentrations were performed at the same process conditions. Samples of feed and permeate from each cycle were taken and analyzed for THF insoluble solids. These results and the recording of masses of each amount of liquid added to or sampled from the feed tank or permeate stream were used to estimate the amount of residual oil left in the concentrate at the end of each cycle. Due to the very similar boiling point curves of the petroleum-based start-up oil and the coal derived liquid, distillation could not be used to directly determine the concentration of residual oil in the concentrate samples.

Experimental Results

Membrane Type Evaluation

Initial process flux characterization experiments were conducted with the two different membrane module types using the diluted coal liquid bottoms. The feed was charged into the system along with one of the membrane modules and the feed was heated in recycle over the course of two days to 265°C. Permeate flux was then measured over the course of several hours at 265°C, 240°C, and 200°C. Transmembrane pressure was 80 psig and the crossflow was about 6 gallons per minute (gpm). Permeate samples were analyzed for non-THF soluble solids. The same process was repeated for the second membrane type. The data for both membrane types are included in Table 1.

Several clear observations can be made concerning the data. First, the 0.01 μm and 0.05 μm membranes were very different in terms of process flux. The 0.05 μm membrane had a very good crossflow process flux of over 200 $kg/m^2/h$ which was a factor of twenty higher than the 0.01 μm membrane. Second, the process flux appeared to be strongly dependent on temperature between 200°C and 265°C. Third, non-THF soluble solids retention was very high for both types of membranes.

Based on the membrane evaluation tests, the 0.05 μm pore size titania membrane was selected for further testing to evaluate the effects of various process parameters on membrane flux performance. The purpose of these parametric tests was to determine the process conditions for subsequent concentration/diafiltration process runs.

Table 1.
Ceramic Membrane Performance in De-ashing of Coal Liquids

Evaluation	0.01 μm Silica		0.05 μm Titania	
Process Flux	Temperature (°C)	Flux (kg/m^2-hr)	Temperature (°C)	Flux (kg/m^2-hr)
	265	11	265	223
	240	5	240	198
	200	1.3	200	98
Solids Retention	> 99.9%		> 99.7%	

Process Variable Evaluation

The data recorded during the process variable evaluation experiments is shown in Table 2. In this table, the permeate flux level is shown to increase by 17% with an increase in temperature from 200°C to 270°C. This increase appears to be small compared to the anticipated increase based on the data obtained earlier in the project (Table 1). Data obtained on a 0.05 μm pore size titania membrane showed an increase of about 120% from 200°C to 265°C. However, the flux performance at about 265°C in both cases was almost the same, 220-225 kg/m^2-hr. The cause for this observation is probably that the first set of data were obtained by heating the feed directly to 265°C then measuring flux performance as the temperature decreased over the course of about 5 hours. In the parametric tests, the 200°C data was taken first and then the feed was heated to 269°C overnight before the flux data at high temperature was taken. If membrane fouling is occurring over time (see below), then the effect of temperature will appear to be enhanced in the first case. Both membrane fouling and temperature decrease will decrease flux thereby making the low temperature flux in the first set of data look very low. In the second case, the high temperature data will have been taken after a longer processing time and the ultimate flux rate due to temperature will not be measured due to membrane fouling. Consequently, the increase in flux due to increased temperature in the parametric test was tempered by time effects possibly as a result of adsorption of materials onto the titania membrane during processing.

The effect of time is more clearly shown in Table 2 between that data taken at 22 hours and 27 hours. With a very small reduction in temperature, the flux falls off by about 45%. It appears that membrane fouling possibly by adsorption of material onto the membrane or plugging of the pores by very fine colloidal material is occurring. The effect of membrane fouling is to reduce permeate flux over long periods of time as flux inhibiting material (foulants) is brought to the membrane via permeation flow. As long as there are foulants in the feed material and they can attach to or plug the membrane, flux will decrease. Membrane modifications or process changes (e.g., feed pretreatment) can have a significant impact on the degree of fouling and should be studied before commercial systems are designed. While membrane fouling is an important process characteristic, it does limit the usefulness of the parametric studies.

Table 2
Coal Liquid Deashing Parametric Studies Using Titania Membrane

Elapsed Time (hrs)	Crossflow (gpm)	Temperature (Deg C)	Average Pressure (psi)	Differential Pressure (psi)	Permeate Flux (kg/m^2-hr)
1.1	5.9	195	77.5	3	193.1
Filter element and feed material slowly heated overnight with no permeate flow.					
22.1	5.8	269	74.0	8	225.7
27.0	6	254	76.0	8	122.8
Transmembrane pressure decreased after 27 hours and allowed to stabilize for four hours.					
31.1	5.9	254	37.5	9	76.8
46.5	6	254	39.0	4	80.2
51.5	5.8	254	38.5	3	67.0
Crossflow decreased after 51.5 hours and allowed to stabilize for 2.5 hours.					
54.3	4	243	39.5	3	56.4
70.7	4	243	37.5	3	45.7

The next process variable evaluated was pressure across the membrane. It can be seen in Table 2 that the permeate flux fell off about 40% with a 50% reduction in the pressure. A large decrease in flux level with reduced membrane driving force is typical for microfiltration applications. However, it is unclear how much membrane fouling contributed to this effect. The relative stability of the flux level over the next 20 hours indicated that the rate of membrane fouling was decreasing. This may occur due to membrane conditioning (i.e., reduction in adsorption sites) and/or a reduction in the amount of foulant in the feed material. Since the experiment is being run with a single batch of material, the foulant could be stripped out of the fluid and onto the membrane. The rate of membrane fouling would decrease as the amount of foulant remaining in the feed is decreased.

Lastly, the effect of crossflow on membrane flux performance was investigated. The effect of crossflow in some applications can be large due to the sweeping action of the fluid across the membrane removing flux inhibiting materials from the membrane surface. As can be seen in Table 1, a 33% decrease in crossflow seemed to cause a 16% decrease in flux. Once again, membrane fouling may have contributed to the observation.

Based on the results of the parametric tests, the process conditions chosen for the concentration/diafiltration runs were those that maximized process flux. These conditions were 270°C, 80 psig inlet pressure, and 6 gpm crossflow.

Diafiltration Process Evaluation

Data from the concentration/diafiltration runs is summarized in Figure 6, 7, and 8 and Table 3. Process flux data from concentration runs 1, 3, and 5 are shown in Figures 6, 7, and 8, respectively. The data is presented using a linear trend line through the flux data points. The trend line is used to give a general guide to the fall off in flux during concentration and is not curve fit to the data which would better indicate the function for flux fall off. The flux data does indicate that each of the concentration run fluxes was fairly similar to each other. This may have been due to the use of start-up oil which is similar to the liquid in the atmospheric bottoms. Use of a lower molecular weight solvent that would need to be pressurized at process temperature but would allow for relatively easy removal from the concentration and permeate by flashing would probably give different results. The overall flux rate is very encouraging. Flux levels for typical crossflow applications range from 20 to 200 l/m^2-hr. Considering the high viscosities and solids concentrations in these streams, the flux levels are very good. This will have a large impact on reducing the number of filters required in a commercial system.

Data in Table 3 includes the measured solids concentration of feed and concentrate samples for each concentration run as well as the calculated amount of residual coal-derived oil in each sample. As can be seen, the amount of concentration that can be obtained with these membrane filters under these process conditions is about 20% solids. Over the course of these concentration runs, most of the residual oil has been extracted from the bottoms. It was calculated that 23% of the oil was removed from the bottoms after 3 dilution/concentration runs while 7% of the residual oil was removed from the bottoms after 5 dilution/concentration runs. This data will be helpful in evaluating the process design and process economics.

Preliminary Process Approach and System Economics

There are many possible locations for a crossflow membrane system to be located in a direct liquefaction process design. These include (1) after the liquefaction reactors, (2) after the atmospheric distillation column, and (3) after the vacuum distillation column. If the system is placed after the reactors, the system will be expensive due to the high temperature and pressure

Table 3
THF Insoluble Solids and Residual Oil Concentrations of Each Process Cycle

	Concentration Runs				
Property	Number 1	Number 2	Number 3	Number 4	Number 5
Feed Solids Conc.	7.2%	9.4%	8.7%	7.8%	7.8%
Retentate Solids Conc.	29.4%	22.1%	17.1%	16.5%	18.8%
Retentate* Residual Oil Conc. (Calc)	62.1%	40.3%	22.8%	11.3%	6.8%

* Residual oil concentration in concentrate calculated on a diluent-free basis. This assumes that in an actual process the diluent would be flashed off leaving only solids and residual oil.

conditions as well as the large volume of liquid to be processed. As a result, CeraMem has performed some preliminary analyses of membrane systems after the atmospheric distillation column with the permeate going to distillate recycle and the dried concentrate going to a gasifier for make-up hydrogen production. In this case the vacuum still and the Rose® unit would be replaced. CeraMem has also looked at replacing the Rose® unit directly by taking the vacuum still bottoms as the feed.

Based on process flows in a 75,000 barrel per day (15,000 tons of coal per day) coal liquefaction plant obtained from Mitre Corporation (McLean, VA) and a permeate flux of 90 liters per square meter per hour, CeraMem has estimated the size and cost of ceramic membrane crossflow diafiltration systems for each scenario. Placing the filtration system after the atmospheric still will require the treatment of a larger process flow, thereby requiring a larger system. Each system would require an estimated 1,535 to 2,500 membrane modules and cost $18,000,000 to $26,000,000. Operating costs (power and membrane replacement) for this type of system is estimated to be about $3,000,000 to $5,000,000. Placing the system after the vacuum still and just replacing the Rose® unit will require a system with an estimated 1,120 to 2,100 modules. The cost for such a system is estimated to be $15,000,000 to $22,000,000 with an annual operating cost of about $2,000,000 to $4,000,000. These estimates do not include associated equipment and further work is required to better define these cost estimates; however, these costs appear to be attractive considering the costs of the vacuum still and Rose® solids removal system for a plant of this size. For example, the capital cost of the Rose® unit for a plant of comparable size has been estimated to be approximately $33,400,000 [1].

Conclusions

Based on work performed to date, CeraMem concludes that 0.05 μm nominal pore size titania membrane crossflow filters can efficiently filter diluted atmospheric flash drum bottoms with excellent solids removal (> 99%) and high fluxes at 270°C (100 to 200 lmh). In addition, a diafiltration process can be designed around these filters. If a relatively volatile diafiltration solvent can be found that is (1) soluble in the coal liquid and (2) capable of being recycled after flashing it off the permeate and concentrate streams, a potentially cost effective MF membrane diafiltration system can be developed.

Future Plans

CeraMem plans on working with Mitre Corporation on further refining the cost estimates for MF membrane diafiltration systems integrated into a direct coal liquefaction process plant. If these costs look attractive, CeraMem believes that additional research to find appropriate diafiltration solvents and experiments on fresh coal liquids from a direct liquefaction process development unit such as the one at HRI would be warranted.

References

1. S. Poddar, P. Adler, and S. Kramer, "Direct Coal Liquefaction - Capital Cost and Economics for Low Rank Coal Design." Proceedings of the Coal Liquefaction and Gas Conversion Contractor's Review Conference, pp. 1-17, September 7-8, 1994.

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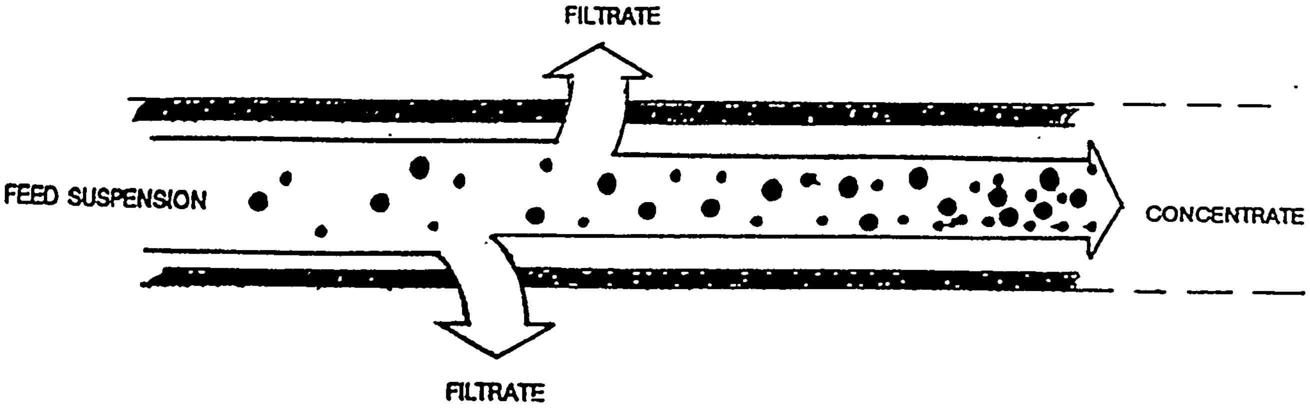

Figure 1. Crossflow Filtration Schematic

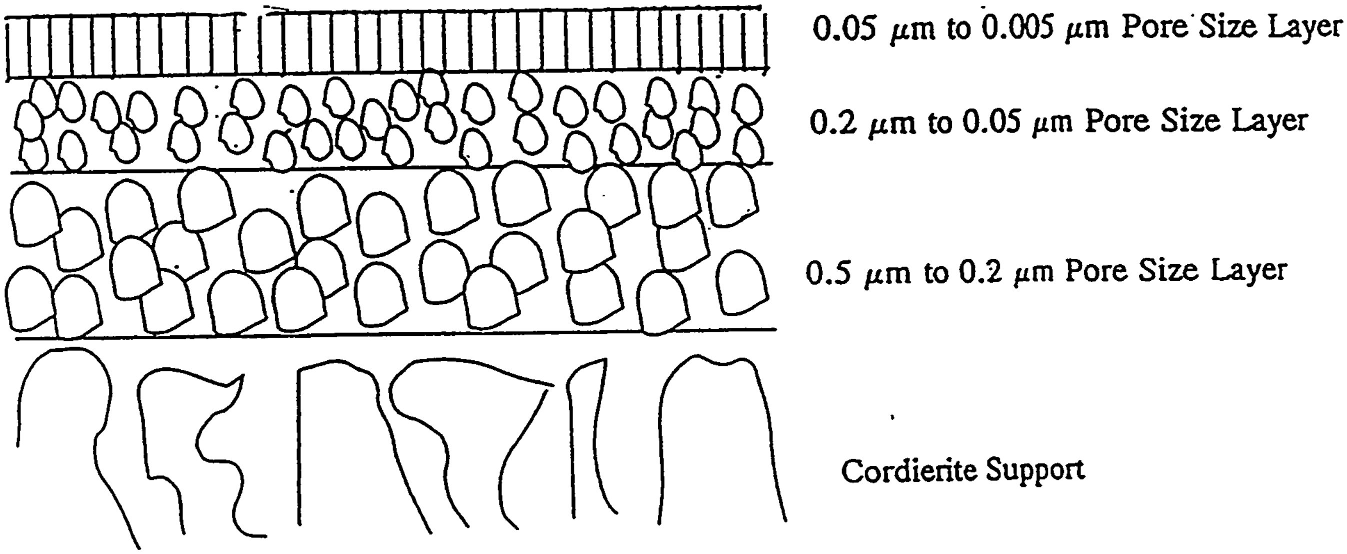

Figure 2. Schematic of Multilayer, Asymmetric Ceramic Membrane

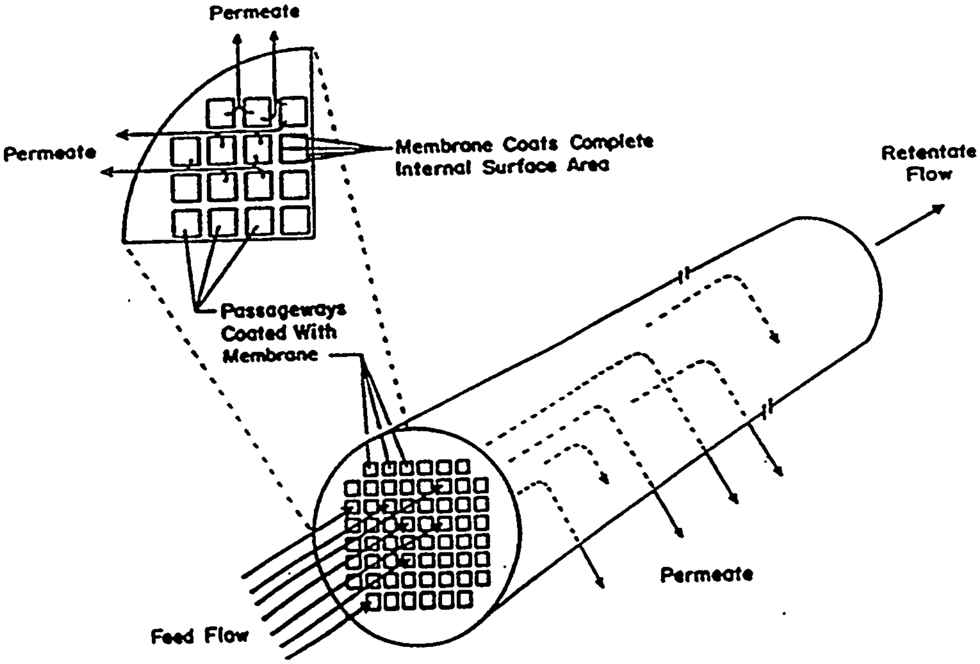

Figure 3. Lab Scale Permeate Flow Schematic

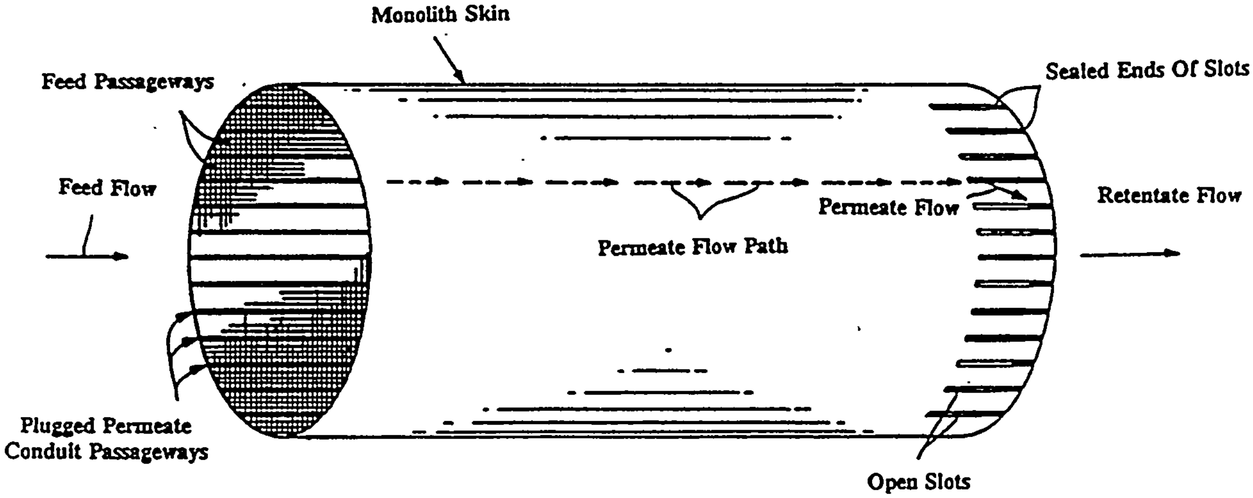

Figure 4. Full Size Permeate Flow Schematic with Permeate Conduits

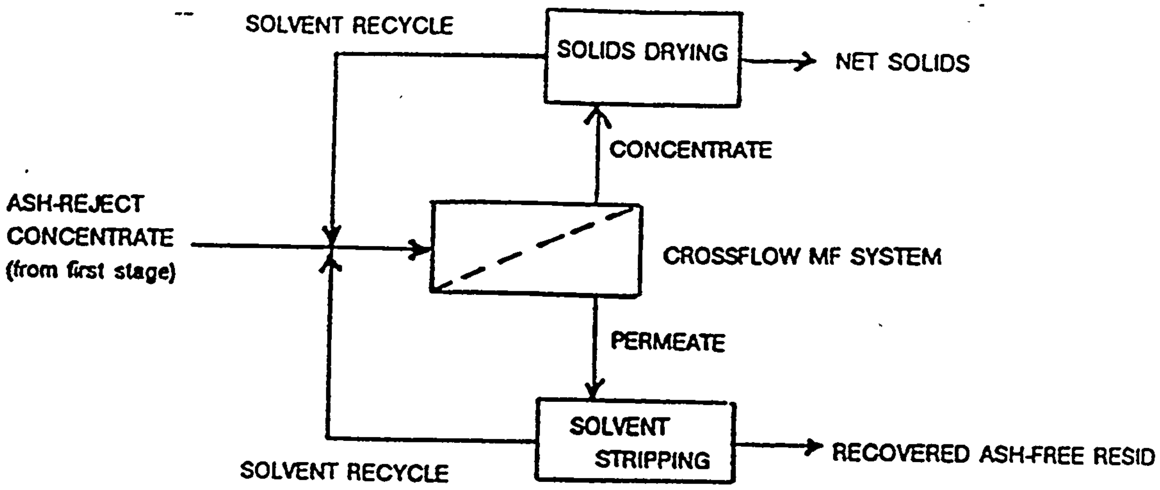

Figure 5. Proposed Deashing Process Using Microfiltration and Diafiltration

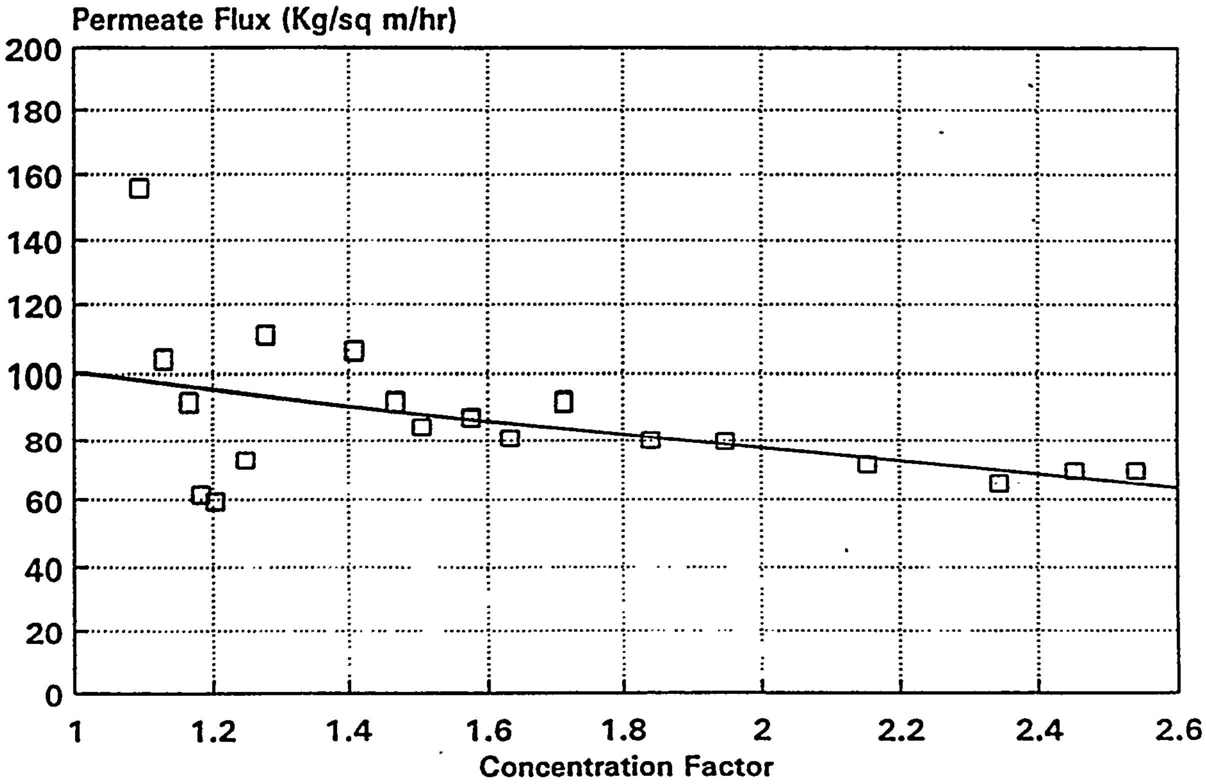

Figure 6. Coal Liquid Process Flux Versus Concentration in Run 1

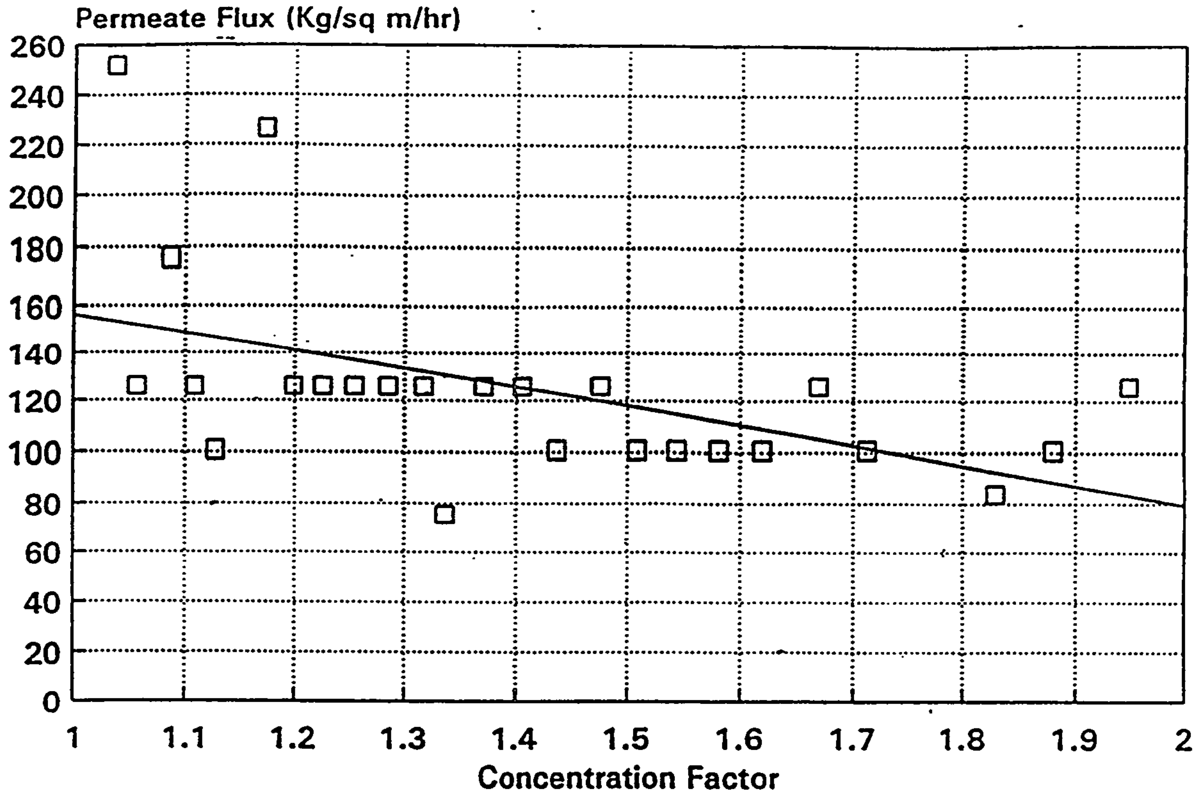

Figure 7. Coal Liquid Process Flux Versus Concentration in Run 3

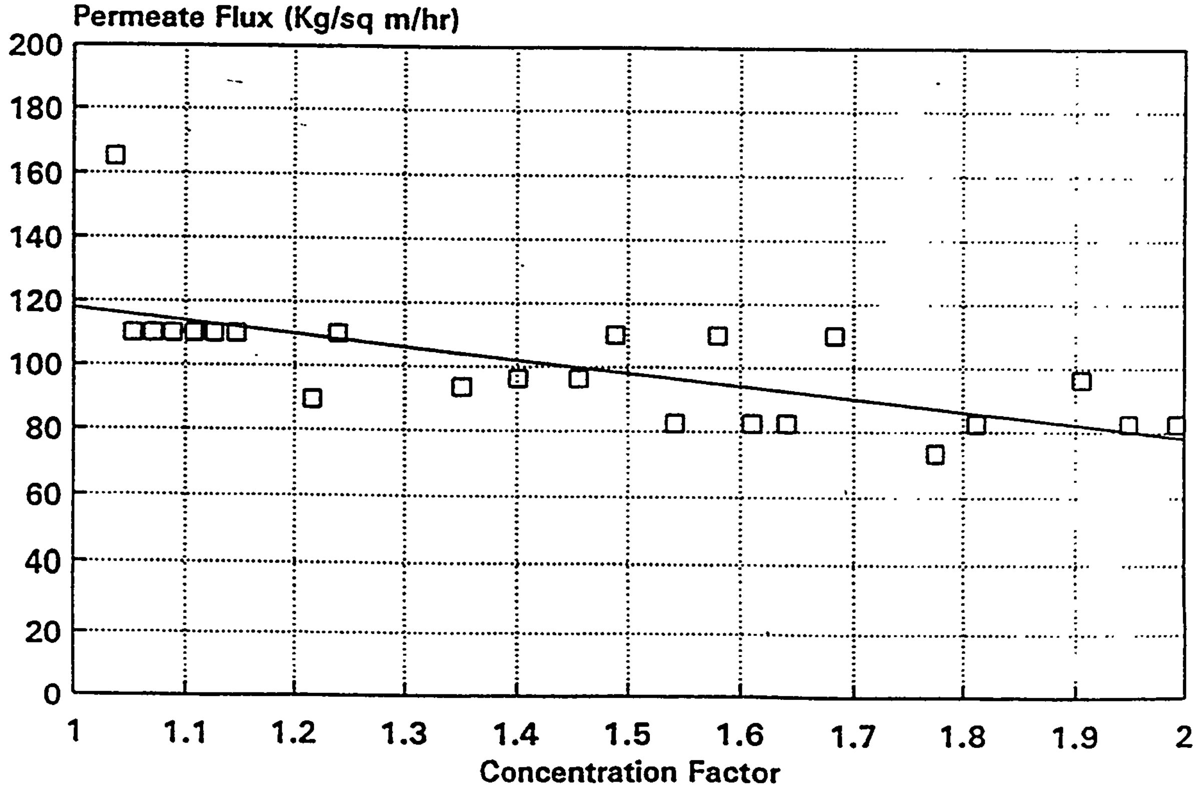

Figure 8 Coal Liquid Process Flux Versus Concentration in Run 5