Section 3

Evaluation of Candidate Processes

The several separation methods identified in Section 2 for further evaluation are reviewed in this section. Each of these methods is examined with respect to equipment requirements and potential cost so that some processes can be recommended for further investigation/testing.

3.1 DENSITY – EXPLOITING WAX/CATALYST DENSITY DIFFERENCE WITH SEDIMENTATION

Sedimentation is a logical choice for a solids separation system, because, if the particles are large enough, the separation can occur fairly quickly and the associated equipment requirements are reasonably inexpensive.

3.1.1 Operating Principles

Settling of single particles is described by both Newton's law and Stokes' law. Newton's law relates to the forces acting on the particle. Stokes' law takes into account the drag forces so that a simple formula exists for the terminal velocity and time of fall as a function of particle and fluid properties. This formula applies to spheres in laminar flow with a Reynolds number of less than 0.3 acting under the forces of gravity. Because one of the parameters is the force of gravity, centrifuging leads to separation by the same process, but with centrifugal body forces, which increase the effective gravitational forces. The formula is:

$$T = (18/G)(\mu/\rho)(L/D^2)$$

where:

T = Fall time, sec

ρ = Particle density, g/cm^3

μ = Viscosity, g/cm-sec

L = Fall distance, cm

D = Particle diameter, cm

G = Effective acceleration, cm/sec^2

The effective acceleration G is given by the formula:

$$G = g(1 - \rho_f/\rho)N$$

where:

g = Acceleration due to gravity, 980 cm/sec^2

ρ_f = Fluid (wax) density, g/cm^3

N = Dimensionless number of g's: $N = 1$ for settling; $N \gg 1$ for centrifuging

Table 3-1 gives fall times for particles of various diameters in sedimentation and centrifuging processes for the STATOIL particle size spectrum shown in Figure 2-2.

Table 3-1 Fall Times for Particles of Various Diameters in Sedimentation and Centrifuging Processes

Defined Particle Size Zone	Zone Increments (wt%)	Cum. Greater Than Zone Bottom Size (wt%)	Zone Top Size (μm)	Zone Bottom Size (μm)	1 g Time to Fall 1 cm (sec)	3,000 g's Time to Fall 1 cm (sec)
1	4	4	40	20	36	0.012
2	16	20	20	10	144	0.048
3	24	44	10	5	575	0.192
4	24	68	5	2.5	2,300	0.77
5	13	81	2.5	1.2	9,981	3.3
6	9	90	1.2	0.6	39,922	13.3
7	6	96	0.6	0.3	159,688	53
8	4	≃100	0.3	0.15	638,753	213
9	0	≃100	0.15	0.08	2,245,617	749

Fall time formula: $T = (18\ \mu L) / (G\rho\ D^2) = (A / B) / (ND^2)$

Effective acceleration formula: $G = Ng\ (1 - \rho_f / \rho)$

Wax viscosity, μ	0.03 g/cm-sec	
Particle density, ρ	4.53 g/cm^3	
Wax density, ρ_f	0.696 g/cm^3	N is number of g's
Fall distance, L	1 cm	D is diameter in cm
Acceleration due to gravity, g	980 cm/sec^2	
Effective density factor $(1 - \rho_f / \rho)$	0.846	
$A = 18\ \mu L$	0.54	
$B = g\ (1 - \rho_f / \rho)\ \rho$	3,757	
A / B	0.000144 sec-cm^2	

Table 3-1 shows that under simple sedimentation, it will take 40,000 seconds (11 hours) to remove 90 percent of the solids (those with diameters greater than 6 microns) when the required fall distance is 1 centimeter. In most large-scale sedimentation systems, however, the fall distance must be greater than 1 centimeter. If the fall distance is 1 inch, the removal time is 1 day. If the fall distance is 1 foot, the required time is 12 days, too long for a practical F-T separation system.

3.1.2 Sedimentation

Sedimentation was used during the 1992 pilot testing when the filtration system did not perform as expected. A tank provided approximately 2 to 4 days of residence time. (This tank may not have been designed with the best features for sedimentation.) Typical sedimentation equipment is shown in Figure 3-1. The wax/catalyst mixture is drawn off from the F-T reactor to, potentially, a chemical mixing tank. Here, chemicals can be added for better settling. The resulting mixture is transferred to the inlet of the sedimentation tank. Sedimentation takes place in this tank with particles of a critical velocity, Vc, settling at the bottom. Smaller particles with a velocity lower than Vc exit in the outlet zone with the majority of the wax mixture. The settled catalyst and some wax are pumped back to the F-T reactor.

The critical velocity, Vc, is the important design variable in sedimentation. Because of the very low velocities (e.g., 0.001 ft/sec) required for sedimentation, everything must be done to minimize stray fluid currents in the settling process. Ideally, the wax/catalyst would not be depressurized, since this could introduce gas formation, which would produce fluid currents. Additionally, the temperature must be maintained by external insulation or heaters so there are no temperature gradients, and the viscosity must not be increased.

Two important design parameters are retention time and rise or overflow rate. Knowing what particles sizes are to be removed enables one to establish a terminal velocity, Vc. Thus, all particles having a velocity equal to or greater than the terminal velocity will be removed. The formula for relating flow quantity Q, surface area of the settling tank A, and critical velocity Vc is:

$$Q = AV_c \qquad \text{[Ref. 5, page 204]}$$

This formula is based upon the retention time, which is equivalent to the maximum amount of time available for the particles to fall.

Typical rise rates, Q/A, are about 0.5 gpm/ft^2 [Ref. 6]. This will be experimentally determined. A cylindrical vessel's diameter with this rise rate using our design case would be:

Diameter = 48 feet

From the particle sizes in Table 3-1, it appears that simple sedimentation is not practical except for removal of the largest particles. Gravity sedimentation could be selected for bulk removal of maybe 20 to 40 percent of the solids, but this would have to be followed by a residual removal system.

3.1.3 Centrifugal Force Devices

For centrifuging at 3,000 g's, however, Table 3-1 shows that it will take only 53 seconds (0.9 minute) to remove 96 percent of the solids (those with diameters greater than 0.3 micron), with a

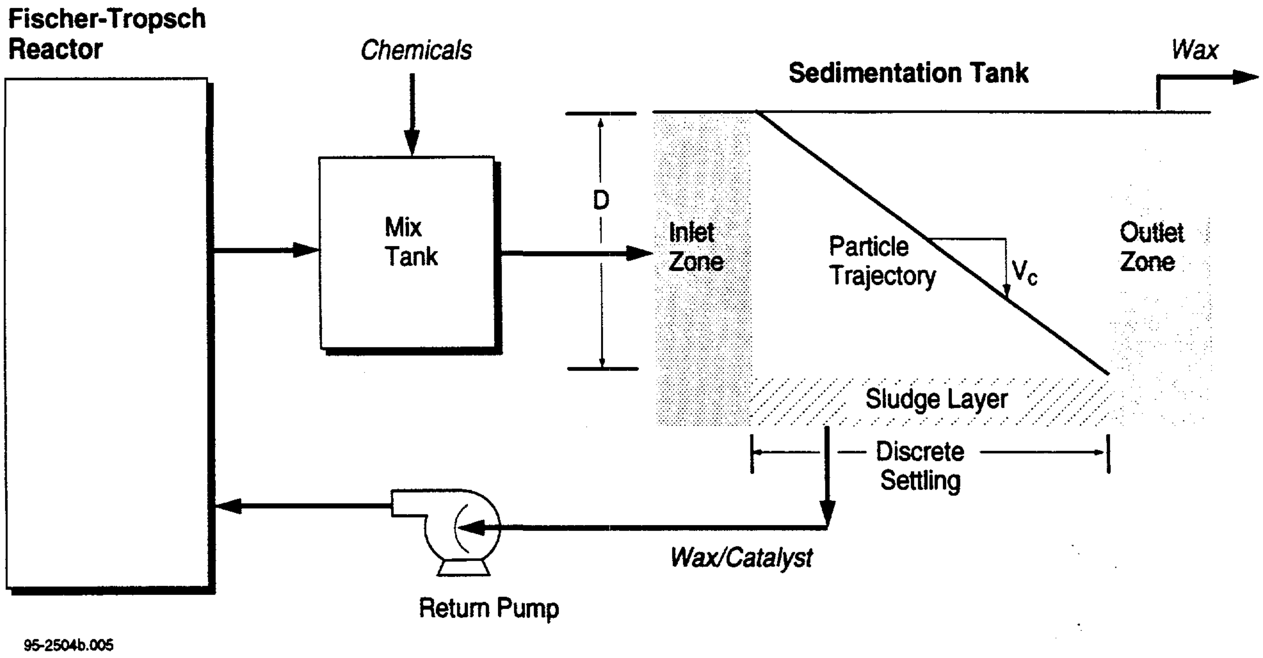

Figure 3-1 Typical Sedimentation Equipment

1-centimeter fall distance. An Alfa Laval continuous centrifuge processing 200 gpm of fluid has a slurry holdup time of about 1 minute and a fall distance of a few centimeters. Accordingly, it seems likely that a centrifuge system can be found that can remove bulk solids.

Vendors were contacted for both hydrocyclones and centrifugal separators (see Appendix 5 for the sample inquiry). Budgetary costs and performance information for a wax production rate of 900 gpm were obtained. A summary of the results follows.

Hydrocyclones

Hydrocyclones would be good for bulk removal and could possibly remove particles down to 5 to 8 microns (50 percent of the solids). This would be a low-capital-cost item. The pressure drop is on the order of 50 to 100 psi so the energy requirements are relatively low. However, a pump would be required to return the wax/catalyst to the F-T reactor. The equipment cost for hydrocyclones is relatively low and was estimated to be $200,000.

Centrifuges

Centrifuges are illustrated in Figure 3-2. The manufacturers estimate that particles whose sizes are less than 2 to 0.5 micron would not be removed. Thus, centrifuges would still not remove the particles to the required purity because of the size distribution. The manufacturers recommend that some testing be done to confirm their budgetary estimates. Also, since some of the manufacturers could have difficulties meeting the operating temperature and pressure requirements, additional development requirements are anticipated. The equipment cost for centrifuges was estimated at $3 million.

3.1.4 Chemical Enhancement

If the catalyst particles can be made larger, then smaller equipment can be used or more efficient removal can be achieved. There is a surface charge on the particles, depending on the material in the particles. When this charge is controlled, the particles can be made to attract each other so that there are larger particles with larger mass, thus allowing better sedimentation. This can be done by addition of chemical, as shown in the chemical addition operation in Figure 3-1. Determining the type of chemicals is largely experimental and must be performed with the constituents expected. Various polymers, including anionic, cationic, and non-ionic, can be used to affect the surface charge.

The following issues can be expected with this type of system:

- *F-T Effect.* Preliminary indications are that smaller particles develop during operation. It may be desirable to maintain these smaller particle sizes. With chemical

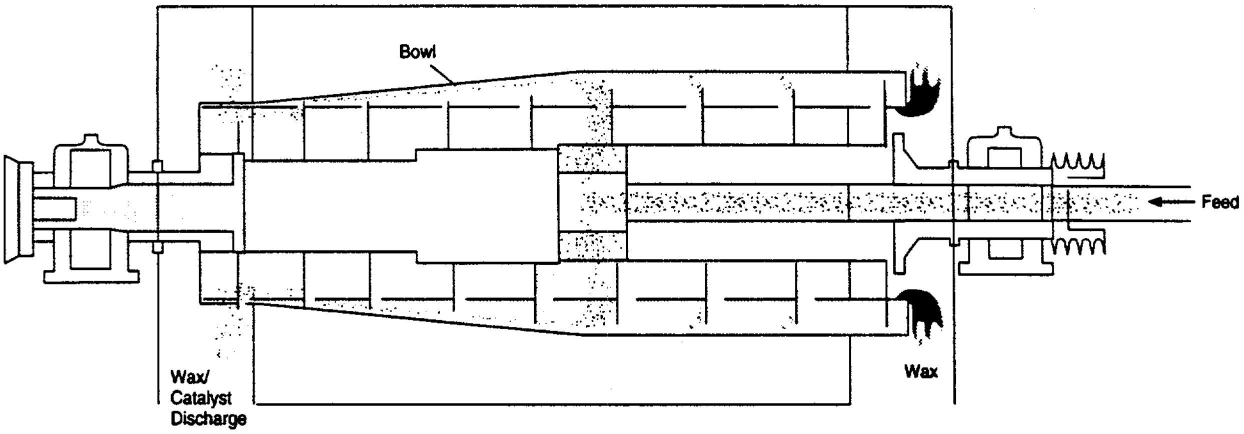

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Figure 3-2 Centrifuge Separation

enhancement, the recovery of the catalyst could lead to buildup of the chemicals in the reactor. This could also affect the performance of the sedimentation process after time.

- *Control.* Controlling the correct amount of the chemical additive is an inexact science. Any changes in the process could cause a corresponding change in the required chemical addition rate or type of chemical.

At this time, Bechtel does not recommend proceeding with the development of this concept. In the event that one of the other processes does not meet expectations, then further work could be done on determining the appropriate chemicals.

3.2 FILTRATION – EXPLOITING PARTICLE SIZE

Filtration is the logical choice for a removal system because it directly blocks passage of particles larger than a certain cutoff size. The DOE program has used filtration as a solids removal technology. The program has revealed a characteristic of many filtration systems that can make them unsuitable for F-T iron catalyst removal, namely, clogging and blindoff due to the large burden of particles smaller than the bulk cutoff diameter. Clogging is most troublesome in filters with long passages of constant pore size (isotropic). The passages should have diameters smaller than the particle cutoff diameter. These filters work effectively if all the slurry solids have sizes larger than the cutoff diameter, which may not be the case with F-T slurries and some filter selections.

There are three approaches to filtration that may be applicable to the F-T requirement:

- Deep-bed filtration
- Filtration with screens (with shallow passages), which can be cleared easily with backflush
- Membrane processes

3.2.1 Deep-Bed Filtration

Some of the available filter system types are summarized in Figure 3-3, taken from Woods [Ref. 4]. The figure shows that submicron solids can be removed by deep-bed filters of a porous medium. Because of the cost to replace spent filter media, such filters work best at very low feed solids concentrations and must be used as residual removal systems following bulk removal by another technology. The question arises whether reasonable filter pressure drops can be achieved for the flow rates expected. This system may be technically feasible for residual F-T catalyst removal, and it should be considered in further studies if other selected methods do not work. A disadvantage of this method is that it permanently removes the smaller particle sizes.

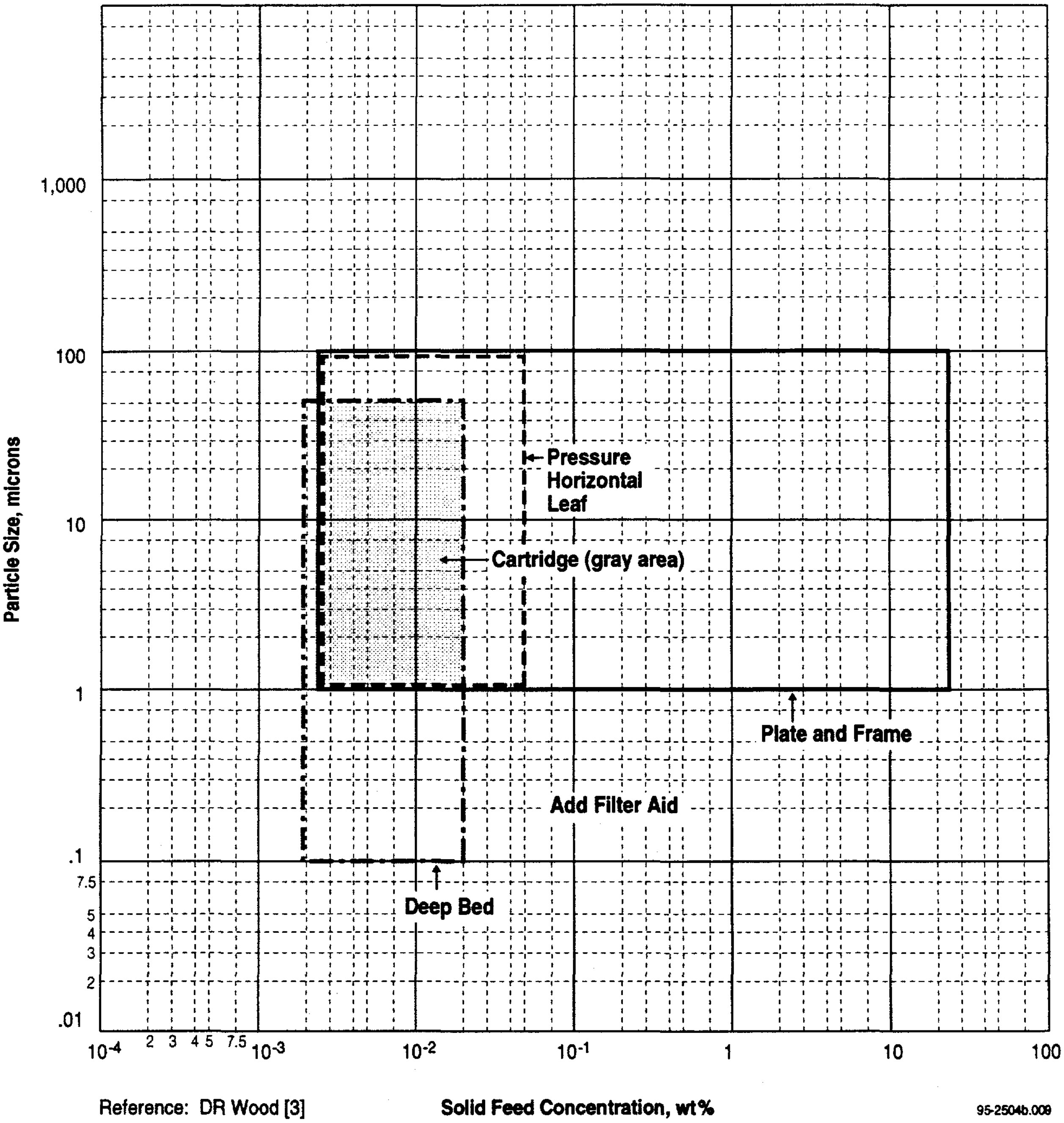

Figure 3-3 General Regions of Liquid-Solid Separation by Filtration

3.2.2 Filtration with Screens

Figure 3-3 also shows that certain plate and frame filters are practical bulk removal systems capable of removing solids as small as 1 micron. The figure also shows additional systems, including cartridge and leaf filters, that could be used as residual removal systems. To the extent that these systems use screens, they are potentially useful. However, to ensure that backflushed solids can clear the filter easily, a screen of such a filter must be one single layer, not several layers, one on top of the other.

The size of the particle that can be removed by either the porous medium or the screen filter can be reduced by the addition of a filter aid. Typical filter aids are diatomaceous earth and expanded perlite. They improve performance of the filter by forming a highly permeable filter cake which can contain the catalyst particles without blinding of the filter surface. The filter aid must be porous, capable of forming a porous cake, and chemically inert, and must have a low bulk density to minimize settling tendency. Filter aids can be added either as a precoat or as a body feed. The body feed requires a continuous addition of a small amount of the filter aid. This traps the catalyst in the filter aid. An additional separation step, however, is required to remove, if possible, the catalysts from the filter aid.

3.2.3 Membrane Processes

One method for separation of the catalyst from the wax is the use of membrane processes. Membrane processes are subdivided into microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO). Either MF or UF could be used since they are both applicable at about 0.1 micron. MF is applicable above this particle size, and UF is more applicable below this size. These approximate areas of application are shown schematically in Figure 3-4. Membrane filters offer the advantages of:

- *Simplicity.* The desired product is separated out while the catalyst is returned to the process. The catalyst stays in suspension, and little or no further mixing is required.
- *Cost.* Because of the simplicity, the cost can be low.
- *Product Purity.* Potentially, a membrane process can achieve the required product purity in one step. Finer size filters are available, if required, to further separate the catalyst and purify the wax.

The primary disadvantages are a lack of theoretical understanding of the process and the lack of success with other filters during earlier testing. Because of its potential advantages, it is recommended that this approach be pursued as the primary method of separation.

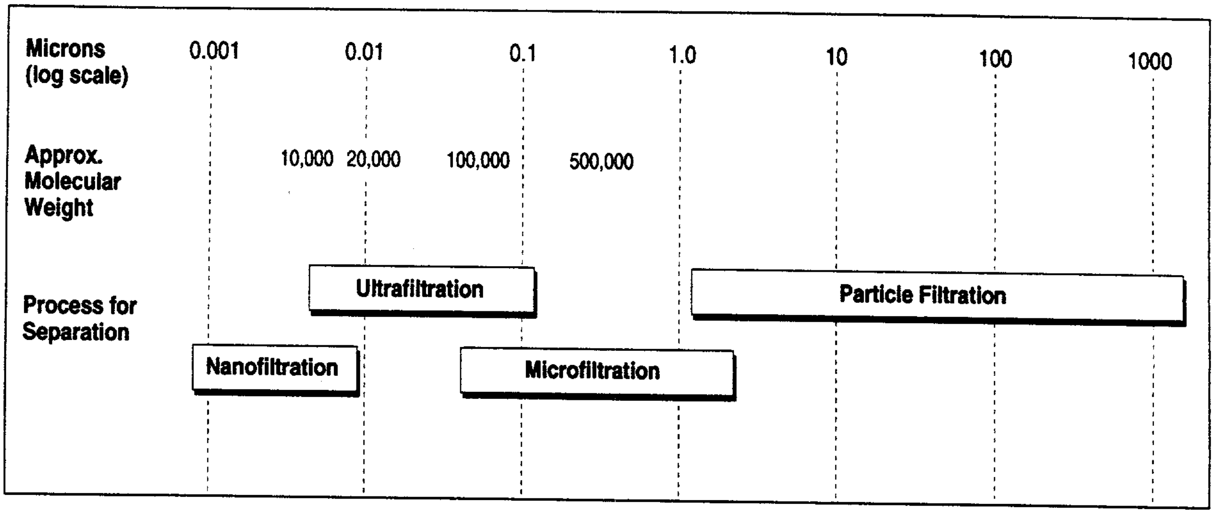

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Figure 3-4 Filtration Classification

3.2.3.1 Membrane Configurations

Membranes come in various configurations depending upon the application. The three most common are spiral wound, hollow fine fiber, and tubular. Tubular and hollow-fine-fiber configurations are most often used with MF. Also, the flow can either be dead-ended (all feed through the membrane) or cross-flow (the feed is tangential to the membrane surface so that only a portion of the feed passes through the membrane). Membrane materials are either organic or inorganic (e.g., ceramic, stainless steel). Because of the high temperatures, inorganic membranes are required for this application.

Membranes can be either asymmetric or isotropic. In asymmetric membranes, the filter is a surface on a porous substrate which provides support for the membrane. In isotropic membranes, the filter is a porous medium which develops a subsurface membrane. The catalyst particles penetrate a short distance into the porous medium to form the membrane. This was the type of membrane provided in the pilot test program. The internal pores are cleaned by periodic backflushing. This regains some of the lost flow.

To understand this operation, one must first understand the principles of membrane separation. Membrane filtration is simple in theory, but very complex in practice, which partly explains why filtration has not reached its full potential. Membrane flux is determined by the pore size, wax characteristics, and clogging from the material in the wax. There are four principal mechanisms of clogging [Ref. 7]:

- Internal pore clogging by plugging with the particles
- Forming of particle deposits on the membrane surface
- The physical adsorption of colloids on the surface or in the pores
- Forming of a polarization layer

These mechanisms can take place independently, simultaneously, or successively. Mathematical modeling of these processes is difficult, but simplified expressions have been developed. Testing is always required to gain an understanding of the way to control the clogging.

Recent studies have shed light on the flux characteristics of cross-flow membranes [Ref. 8]. The important parameters were summarized in Table 4 of that reference. They are:

- *Suspension pH.* More important with smaller particle size
- *Cross-Flow Velocity.* Higher velocities do not always increase the flux
- *Particle Shape.* Has a significant effect on flux

- *Suspension Concentration.* Higher concentrations generally gave low fluxes but equilibrium was established more quickly
- *Filtration Pressure.* Significantly increased flux with larger particles but was less significant with smaller particles and higher concentrations

3.2.3.2 Previous Wax/Catalyst Testing with the Mott Filters

The earlier Mott laboratory testing performed for DOE was reviewed to better understand what went wrong, with a view to improving the filter system. This revealed the following:

- The Mott filter is a cross-flow isotropic filter which builds up a finer filter opening by forming a membrane from the flowing material. Because the medium is isotropic, some particles can become entrained in the filter (see Figure 3-5). This design requires frequent backwash.
- The testing probably did not simulate the actual fluids well because the catalyst size distribution differed sharply (Figure 2-2) from that of the design catalyst
- Particle size distribution appeared to decrease during the testing, possibly as a result of precipitation or mechanical forces
- Surface fouling was observed. This could be due to iron precipitate, which forms iron hydroxide (pH, temperature, and oxygen are the key parameters of iron hydroxide formation). Operation was satisfactory during the first day of testing, but changed substantially overnight

Future test procedure development should include the following:

- Establish criteria for size distribution of the particles and the most desirable size to retain in the reactor (which in turn will help determine the appropriate process). Use the design case (STATOIL) size distribution, shown in Figure 2-2, in the testing
- Understand the factors affecting the iron catalyst during plant operation and during laboratory testing. The catalyst is composed of ferric and ferrous iron, which affects the type of precipitates that can result. Ferrous iron can be oxidized by air to form iron hydroxide [Ref. 9], particularly at higher temperatures, as during the laboratory testing. This forms a gel-type precipitate that is much more difficult to filter than solid particles. The understanding of associated reactions is also important since it affects the pilot test planning
- Determine how and why the particle size distribution changes
- Include in the design criteria information on the presence or absence of oxygen and the pH of the fluid (lab testing should include the same criteria)
- Review related separation projects in de-ashing of coal liquids where preliminary testing using MF ceramic membranes is under way [Ref. 10]

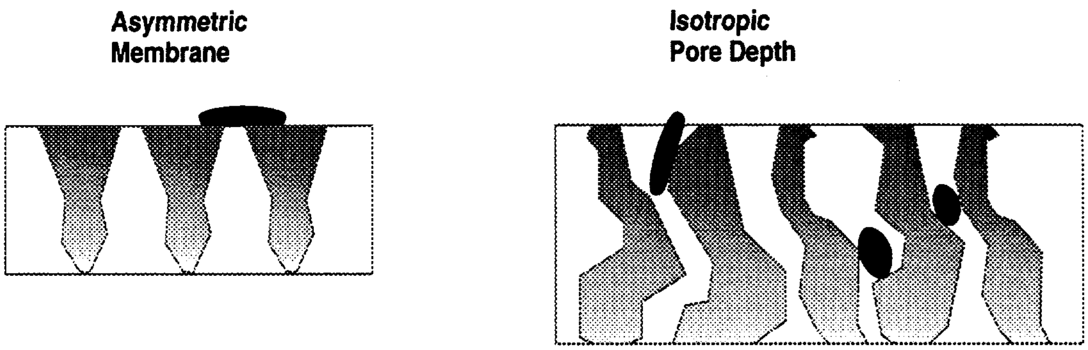

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Figure 3-5 Asymmetric and Isotropic Filter

- Consider the use of asymmetric membranes for the separation
- Evaluate the advantages of testing other membranes in addition to the Mott membrane filters

3.2.3.3 Membrane Treatment System

Conceptual Design

A conceptual design for an asymmetric membrane system was specified as shown in Figure 2-3. It involved bulk separation before the residual membrane separation. This bulk separation was included as an aid to the membrane filter, if required. This conceptual design, along with design values for sizing the system, was given to membrane manufacturers for comment and cost estimates.

Design Selection

Manufacturers of inorganic, asymmetric membranes were contacted, including Osmonics, Carre/Graver, Norton/Millipore, Alcan Separations, and Pall Corporation. Both Osmonics and Carre/Graver responded.

The manufacturers recommended not using a bulk filter at this time. Thus, the configuration as shown in Figure 2-3 without a bulk removal would be adequate. Both manufacturers recommended testing before a finalized cost is determined. However, preliminary estimates of this cost were supplied.

Cost

The Graver Separations, Inc. estimate of the cost of the equipment is $2.5 million and is based upon a membrane flux of 100 gpd/ft^2 (0.069 gpm/ft^2). Since this is a lower flux than the 0.2 gpm/ft^2 measured during the first day of Mott pilot testing, the Graver estimate is regarded as possibly conservative. This capital cost includes pumps, membranes, membrane housing, and piping.

3.3 ENHANCED SEDIMENTATION – EXPLOITING VISCOSITY-REDUCING ADDITIVES – EXPLOITING COAGULANTS

Fall time is directly proportional to the fluid viscosity and inversely proportional to the square of the particle diameter. Accordingly, shorter fall times in both gravity systems and centrifuges can be obtained by reducing fluid viscosity by addition of a low-viscosity solvent, and by increasing particle size by coagulation. This process requires an additional separation step to remove the added solvent.

3.4 HIGH-GRADIENT MAGNETIC SEPARATION (HGMS) – EXPLOITING MAGNETIC SUSCEPTIBILITY

Under the leadership of personnel at Aquafine Corporation in Georgia, HGMS has been used commercially since the early 1970s to separate components on the basis of differences in magnetic susceptibility. The first major application involved removal of iron-stained particles of kaolin from unstained particles to produce a white clay additive for certain grades of paper. Additional applications include purification of water, cleanup of oils, processing of metallic ores, and removal of ash and pyrites from coal.

In 1983, Aquafine performed for EPRI a definitive study of several separations that were of interest to the power industry. The study showed how cost varied with components and the required degree of separation.

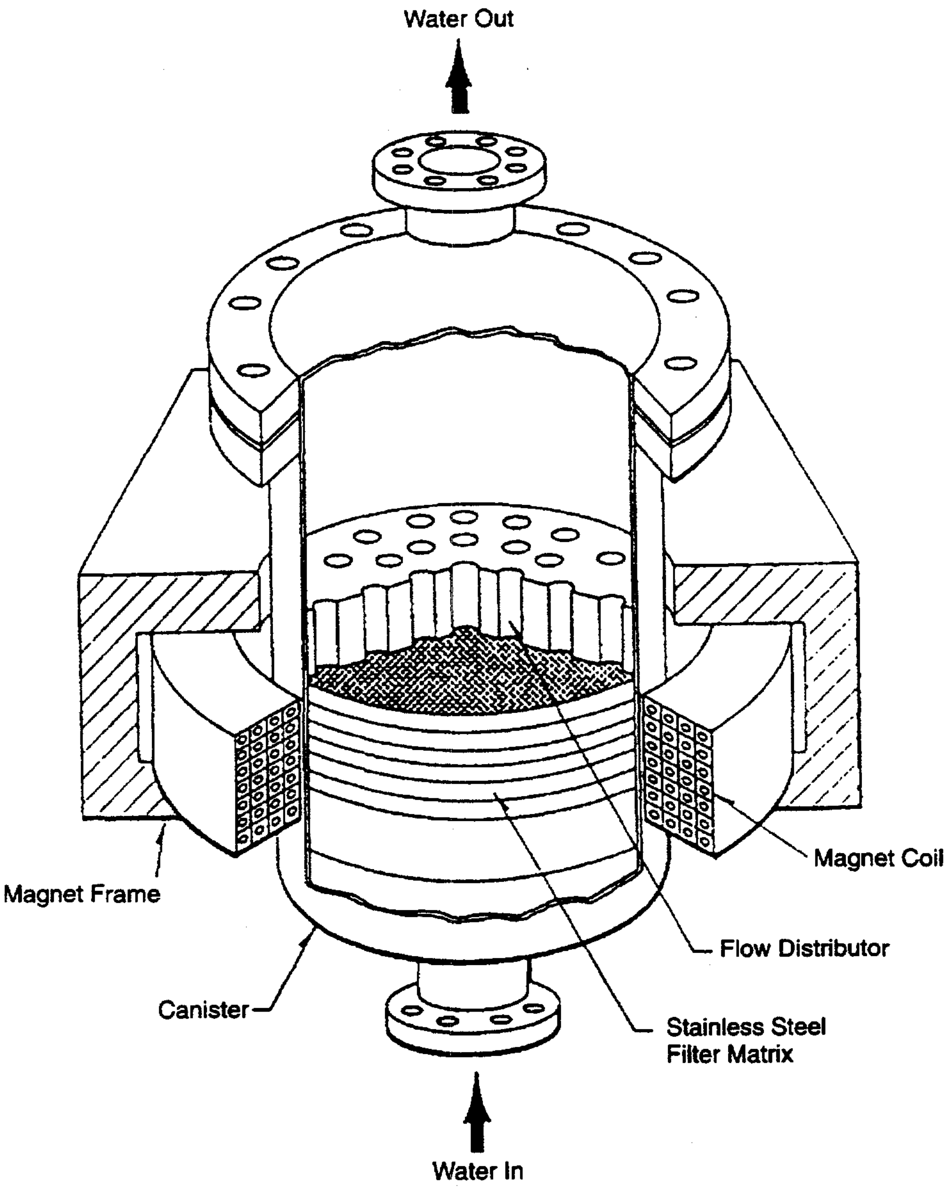
Iron oxide F-T catalysts in principle are excellent candidates for separation from slurry wax, since iron oxide is at the upper end of paramagnetic susceptibility, while wax has negative magnetic susceptibility. Solids containing considerably less iron oxide than F-T catalysts have been successfully separated from other components by HGMS. A major advantage of HGMS for F-T wax/catalyst separation is its stainless steel capture medium whose very high void fraction (95 percent) prevents clogging by ultrafine particles. This is shown in Figure 3-6.

Aquafine Corporation predicts that HGMS would be a practical method of removing F-T particles down to less than 0.1 micron size, leaving 2 to 5 ppm of solids in the product wax. The separation would be carried out with bulk and residual removal units in series. Budgetary equipment costs are estimated to be $20 million for 900 gpm. This system would require two trains, each of which would include one HGMS unit for bulk separation followed by a second unit for fine filtration.

HGMS appears technically feasible and should be considered further because it can remove the very fine particles. However, testing would be necessary to confirm equipment operation at the temperatures and pressures required. The effects of changing properties of the catalyst should also be investigated further. If as discussed in the work on catalyst properties [Ref. 3], the particles change to a more nonmagnetic form, the performance could be degraded and the process could become unsuitable.

3.5 MODIFIED KERR-McGEE PROCESS

A separation system that combines centrifuging with the use of a low-viscosity thinning solvent would be an innovation worth examining further. Any liquid reaches its lowest viscosity at its critical temperature. At slurry reactor exit conditions, heptane is at its critical temperature and its critical viscosity is 0.026 cp (the slurry is 115 times as viscous). Mixing in 50 percent heptane



Type B – Section of Stainless Steel Wool Filter (8).

Reference: "Evaluation and Optimization of Magnetic Filters on Simulated Boiler Water," EPRI NP-3273, November 1973

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Figure 3-6 Aquafine Magnetic Filter

should reduce the mixture viscosity to 0.66 cp (22 percent of slurry viscosity) according to the Kendall-Monroe mixture viscosity equation (the cube root of the mixture viscosity equals the weighted average of the cube roots of the components). The effect of this on fall time is equivalent to more than doubling the particle size.

The feasibility of this process should be investigated further, perhaps in consultation with Kerr-McGee.

3.6 COMPARISON OF SEPARATION PROCESSES

A comparison of the processes is shown in Table 3-2. Bulk removal of up to 50 percent of the catalysts can be achieve inexpensively by several of the processes. However, only the filtration process using membranes can separate the wax/catalyst in one operation.

Table 3-2 Comparison of Separation Processes

Process	Capital Cost	Suitable for:			Recommendation	Comments
		Bulk	Residual	Both		
Kerr-McGee ROSE	High		X		Backup design after modifications	Baseline design, may not work with present particle distribution
Sedimentation	Medium	X			Drop	Large insulated pressure vessel
Hydrocyclone	Low	X			Determine if it enhances membranes	Possible wear of the hydrocyclone
Centrifuge	Medium		X		Drop	Does not meet product purity
Coagulation/ filter aids	Low		X		Consider for polishing filter if required	Either lost catalyst or separation of chemical/catalyst requirements
Porous medium	Low		X		Drop	Lost catalyst
Screen filters	Low	X			Drop	Lost catalyst
Membrane filters	Low			X	Testing	Experimentation required
HGMS	High	X	X		Test if others fail	Demonstration required
Chemical enhanced sedimentation					Drop	Additional complications and chemical separation

Membrane filters, particularly the Mott filters, should be studied further.