Microfiltration of Nickel Powder
in Kerosene

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ABSTRACT

A crossflow microfiltration study was carried out for the separation of nickel powder from kerosene. This study is part of preliminary work for the evaluation of a membrane reactor system for the hydropurification of diesel fuels using glassy alloy particulates as catalysts. This portion of the study was to determine the effects of operating parameters namely trans-membrane differential pressure, feed cross-flow rate, and fines loading %. A statistical design software was implemented for the correlation of results and prediction of optimum conditions for a given separation. The results obtained indicated that there were factors which must be considered, including improvement to the design of the microfiltration system.
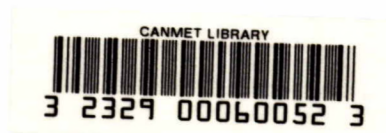
INTRODUCTION

This work was performed as part of a project to evaluate glassy metal alloys for their catalytic properties along with a suitable reactor design to contain small sized powders of the alloys in a hydrogenation reactor. The anticipated small size of the catalyst particles, 1 to 10 μm, suggests the use of a slurry reactor in combination with a microfiltration system capable of operation at the reactor conditions to retain the catalyst. For this reason, a ceramic membrane that can operate at these conditions was selected. To simulate the catalyst, nickel powder was selected, because of its size range and its density. For convenience, ambient operating conditions were chosen for the microfiltration experiments.

The goal of this work is to determine any limitations on the recovery of catalyst that could alter the strategy of using unsupported glassy metal alloys in combination with microfiltration.

EXPERIMENTAL

Membranes

The membrane used for the microfiltration experiments was a Membralox[*] laboratory scale ceramic membrane and was obtained from Alcoa Separations Technology Division. The membrane element was of a tubular configuration having an inner diameter of 7mm and a length of 250mm. The material of construction was alpha alumina having a pore size rating of 0.2μm. The membrane housing was obtained from Alcoa Separations Technology Division as well.

Microfiltration Test Apparatus

A system for microfiltration as a batch process was constructed as shown schematically in Figure 1. The membrane unit was incorporated into the system in a crossflow arrangement. A positive displacement progressive cavity pump provided the circulation of the feed mixture across the membrane surface as well as the driving pressure forcing permeate across the membrane. It will be noted that the packing used to seal the rotor of the pump was a braided teflon and graphite packing. The permeate from the membrane was recycled back to the feed reservoir. Regeneration of the membrane at the end of each run was achieved by backflushing the permeate through the membrane using a gear pump which provided a pressure of 65 psig on the permeate side for two (2) minutes. The pressure on the feed side was reduced to approximately 0 psig during the backflush cycle.

Feed Composition

Kerosene type 1-K was obtained from Canadian Tire Corporation and nickel powder of particle size between 200 and 325 mesh was obtained from Dr. L. Collins

of Metals Technology Laboratories of the Mineral and Energy Technology Sector of Energy, Mines and Resources, Canada. The feed mixture consisted of 7.5 litres of kerosene and appropriate masses of nickel powder to give mass of nickel to volume of kerosene ratios at 25 °C as given in Table 1. This mixture was introduced into the feed reservoir.

Experimental Design

"Design Expert", a statistical design software package available from Stat-Ease Inc. was utilized to select experimental parameters for the input experimental variables. The variables selected to be of importance were feed circulation rate, nickel powder content (wt/vol @ 25°C) and trans-membrane differential pressure (ΔP). The parameters as determined by the statistical design are given in Table 1.

Microfiltration experiments

For each set of variables specified by the experimental design software two microfiltration tests were performed. The duration of each test was fifteen (15) minutes with measurements of operating pressure, feed circulation rate and permeation rate measured at intervals of five (5) minutes. After each test samples of permeate and rejected feed were taken and the membrane was backflushed as described earlier in order to regenerate the membrane and to empty the permeate reservoir for the next run. All tests were performed at 40 °C.

Analysis of Fines

Samples of feed and permeate were analyzed for fines content. Samples were allowed to settle and kerosene was decanted off in order to weigh the nickel powder which was present. For samples which did not separate so easily, particle concentration was determined by visible absorption techniques using a Horiba model CAPA-500 particle size analyzer, and a Milton Roy Company Spectronic 21 visible spectrometer. Procedures for each instrument were carried out as specified in the respective manuals using kerosene as a blank. Comparisons were performed, using as standards, nickel powder sieved in the range of 200 to 325 mesh and graphite powder which passed through a sieve of 400 mesh.

RESULTS AND DISCUSSION

The experimental data obtained for the microfiltration of nickel powder from kerosene are given in Tables 2 and 3. The wt % nickel in the feed is tabulated in two columns in both tables. The column with the heading "statistical design" represents the wt % of nickel based on the mass of powder and kerosene placed into the feed reservoir. The column of heading "actual" is the wt % nickel determined gravimetrically in the feed at a point in the system immediately after the membrane element. As tabulated in both Tables 2 and 3, the concentration of nickel in the feed reaching the membrane in the system was essentially 0 for all experiments performed. It is assumed that mixing of the nickel and kerosene in the reservoir based on the turbulence provided by the recycling of the feed is insufficient in providing a uniform mixture.

Table 2 tabulates the rate of permeation across the membrane. The permeation rates were found to decrease for each test over time including the test having zero wt % nickel in the feed. In most cases the rates of permeation were restored after a backflushing cycle. Analysis by statistical design relating the operating parameters to the permeation rate at time zero resulted in little correlation.

Analysis of the feed and permeate streams by visible absorption methods indicate that there were traces of compounds other than those of kerosene in both streams for all samples. Analysis over time using the Horiba model CAPA-500 particle size analyzer showed that the matter foreign to kerosene appeared to settle out slowly, at a much slower rate anticipated for nickel powder. A possible source of contamination in the microfiltration system is carbon in the form of graphite which is a component of the packing material for the rotor of the progressive cavity pump.

With the assumption that graphite was present as the sole contaminant in the kerosene samples taken from the feed and permeate, a particle size analysis using the Horiba CAPA-500 of the feed of run number 12 is shown in Figure 2. A particle size distribution of graphite was found to be in the range of 0.5 to 4.0 μm. A particle size analysis of the corresponding permeate showed that there was no particulate present. However, visible absorbtion analysis at 400 nm using the Milton Roy Company Spectronic 21 visible spectrometer did reveal contamination in the permeate, which introduces doubt into the completeness of the particle size analysis as carried out by the CAPA-500 analyzer.

Assuming all contamination detected by the Spectronic 21 spectrometer was due to the presence of graphite, all feed and permeate samples were quantified for graphite as given in Table 3. Since concentration of contaminant in the permeate was approaching the lower limit of detection for the Spectronic 21 spectrometer (0.0003 wt % in kerosene), the results calculated for the rejection of graphite by the membrane are scattered, thereby making it difficult to recognize any trends. However, the average rejection of graphite by the 0.2 μm

membrane was 74 ± 5 %.

Due to the low sensitivity of the Horiba CAPA-500 particle size analyzer it is difficult to determine the particle sizes of particles rejected and permeated. However, given the data available and assuming that the contaminant present in the microfiltration system was graphite, it is highly likely that the particle size distribution was of the same order of magnitude as the pore size range of the membrane pores. This would also support the observation that the membrane element was slowly fouled throughout the duration of each test as indicated by a reduction in the rates of permeation.

As stated earlier, the fouling of the membrane was found to be reversed by backflushing the membrane periodically. The membrane was not equally regenerated after each test. The regeneration of the membrane appeared to be most incomplete, and permanently affected after run number 3 in which a ΔP of 50.5 psi was applied across the membrane. This was the first test in which a ΔP of that magnitude was encountered. The two previous runs which employed ΔP's of 36.5 and 25.5 psi were followed by backflushing which appeared to completely regenerate the membrane. Since the backflush pressure utilized was 65 psig, it is assumed that a backflush pressure of approximately two times the magnitude of the ΔP would be required to completely regenerate the membrane.

Although the rates of permeation were affected by the extent of regeneration of the membrane, close examination of the permeation rates in Table 2 indicates that the pressure drop (ΔP) across the membrane had a great affect. The circulation rate of the feed was not found to have a large impact on the product rates across the membrane.

CONCLUSION

Although the original objectives of this study were not reached, much useful information for the fabrication and operation of a microfiltration apparatus were obtained.

For uniform mixtures of nickel and kerosene to be maintained in a microfiltration apparatus, it is recommended that more aggressive mixing techniques in the feed reservoir be employed, such as the use of a mechanical stirrer. Turbulence resulting from the circulation of the feed back into the reservoir was shown to be insufficient. It is recommended that no further microfiltration experiments be performed without improved stirring.

Contamination from all sources must be minimized. It is believed that the braided teflon and graphite packing sealing the feed circulation pump was the source of contamination detected in the feed and permeate. It is recommended that this packing be replaced with a teflon "food grade" packing.

Backflushing may be a necessary component in the design of microfiltration experiments utilizing ceramic membranes. It is recommended that a pump be employed which is capable of delivering pressures at least two times the magnitude of the pressure differentials (ΔP) used in further microfiltration work.

From the results obtained in this work, it appears that the permeation rate is highly dependent on the pressure differential across the microfiltration membrane, and not highly dependent on the feed circulation rates.

One final consideration into the design of further microfiltration experiments is the manner in which the permeate is recycled back to the feed mixture. The permeate in this study was returned to the feed reservoir in order to continue studies on the same mixture without depleting or changing the composition of the feed. However, samples of permeate were removed continuously for analysis, thus concentrating the particles in the feed, and possibly changing the particle size distribution. This must be taken into consideration for the planning of further work so that precautions may be taken to avoid unintentionally altering the composition of the feed mixture.
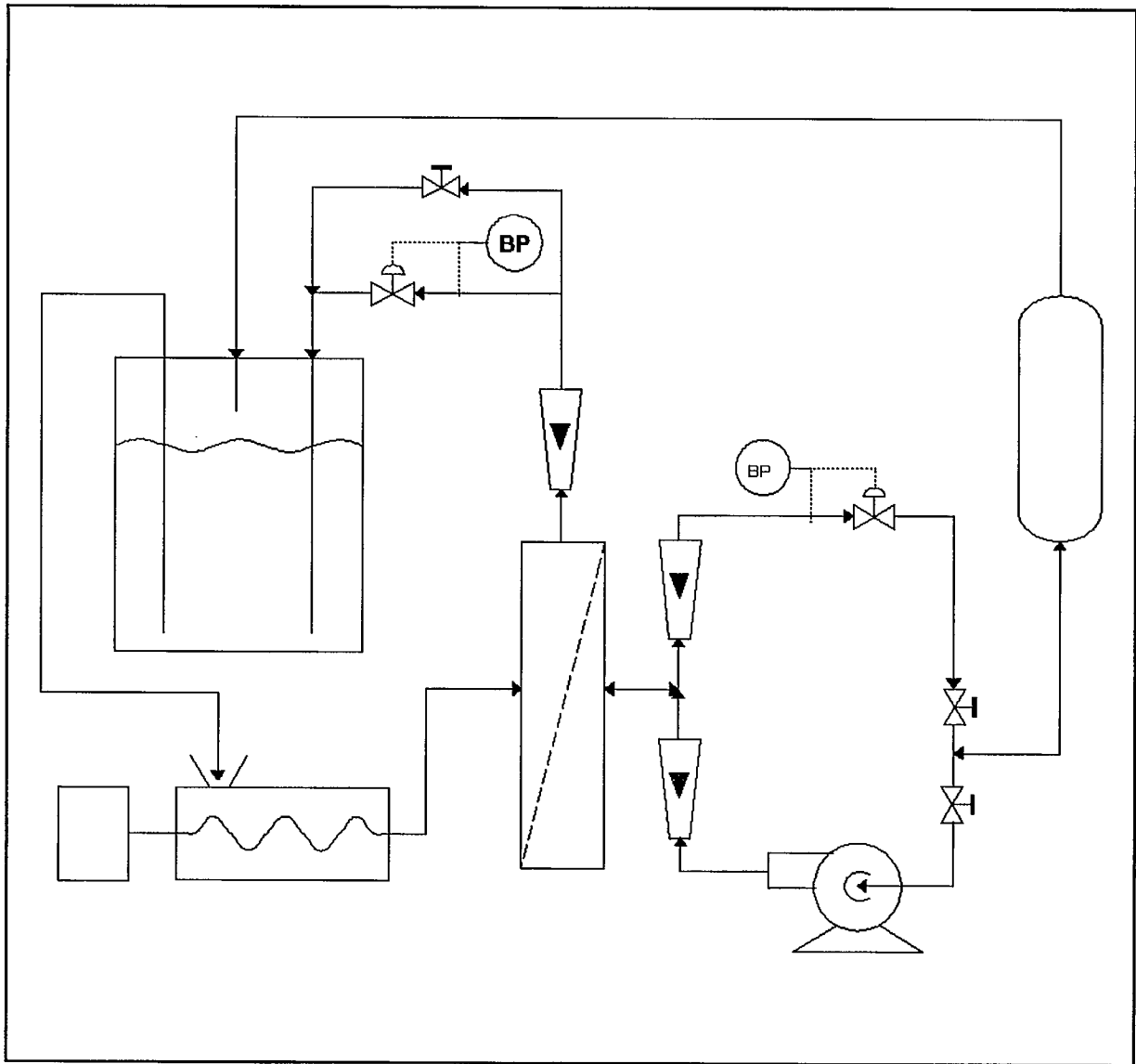
Figure 1 – Schematic diagram of microfiltration apparatus

Table 1 – Experimental parameters suggested by experimental design software

Run Order	Pressure Differential (psi)	Circulation Rate (L/min)	Solids (wt %)
1	25.0	8.0	0.5
2	37.5	5.5	1.5
3	50.0	8.0	2.5
4	37.5	5.5	1.5
5	25.0	3.0	2.5
6	37.5	5.5	1.5
7	37.5	5.5	1.5
8	16.5	5.5	1.5
9	58.5	5.5	1.5
10	37.5	5.5	0.0
11	37.5	5.5	1.5
12	50.0	3.0	0.5
13	25.0	3.0	0.5
14	50.0	8.0	0.5
15	37.5	9.7	1.5
16	50.0	3.0	2.5
17	37.5	5.5	1.5
18	25.0	8.0	2.5
19	37.5	5.5	3.2
20	37.5	1.3	1.5

Table 2 - Permeation rate data obtained from microfiltration of nickel/kerosene mixtures

Run Order		ΔP	Circ Rate	Solids (wt % Nickel)		Permeation Rate (mL/min)			
Actual	Stat Design	(psi)	(L/min)	Stat Design	Actual	0 min	5 min	10 min	15 min
1	10	36.5	6.3	0.0	0	250	200	175	175
2	1	25.5	8.3	0.5	0	175	100	50	50
3	12	50.5	3.8	0.5	0	225	175	100	50
4	13	25.5	3.8	0.5	0	50	50	<50	<50
5	14	50.0	8.3	0.5	0	175	100	50	50
6	2	36.5	6.3	1.5	0	50	50	<50	<50
7	8	16.5	6.3	1.5	0	<50	<50	<50	<50
8	4	36.5	6.3	1.5	0	50	50	50	50
9	7	36.5	6.3	1.5	0	50	50	50	<50
10	9	58.5	6.3	1.5	0	100	100	50	50
11	6	36.5	6.3	1.5	0	50	50	50	<50
12	15	37.5	9.3	1.5	0	50	50	<50	<50
13	11	36.5	6.3	1.5	0	50	<50	<50	<50
14	20	38.5	3.0	1.5	0	50	<50	<50	<50
15	17	37.5	6.3	1.5	0	50	50	<50	<50
16	3	50.5	8.3	2.5	0	150	100	50	50
17	5	25.5	3.8	2.5	0	50	<50	<50	<50
18	16	50.5	3.8	2.5	0	50	<50	<50	<50
19	18	25.5	8.3	2.5	0	<50	<50	<50	<50
20	19	37.5	6.3	3.2	0	50	<50	<50	<50

Table 3 - Solids content data obtained from the microfiltration of nickel/kerosene mixtures

| Run Order | | ΔP | Circ Rate | Solids in Feed (wt % Nickel) | | Solids (wt % Graphite) | | Rejection of Graphite |
Actual	Stat Design	(psi)	(L/min)	Stat Design	Actual	Feed	Permeate	(% wt)
1	10	36.5	6.3	0.0	0	0.0028	0.0008	71
2	1	25.5	8.3	0.5	0	0.0024	0.0008	67
3	12	50.5	3.8	0.5	0	0.0028	0.0009	68
4	13	25.5	3.8	0.5	0	0.0029	0.0007	76
5	14	50.0	8.3	0.5	0	0.0034	0.0009	74
6	2	36.5	6.3	1.5	0	0.0032	0.0008	75
7	8	16.5	6.3	1.5	0	0.0029	0.0008	72
8	4	36.5	6.3	1.5	0	0.0030	0.0008	73
9	7	36.5	6.3	1.5	0	0.0030	0.0012	60
10	9	58.5	6.3	1.5	0	0.0033	0.0007	79
11	6	36.5	6.3	1.5	0	0.0035	0.0008	77
12	15	37.5	9.3	1.5	0	0.0037	0.0008	78
13	11	36.5	6.3	1.5	0	0.0035	0.0008	77
14	20	38.5	3.0	1.5	0	0.0040	0.0009	78
15	17	37.5	6.3	1.5	0	0.0039	0.0009	77
16	3	50.5	8.3	2.5	0	0.0041	0.0011	73
17	5	25.5	3.8	2.5	0	0.0034	0.0008	76
18	16	50.5	3.8	2.5	0	0.0039	0.0009	77
19	18	25.5	8.3	2.5	0	0.0038	0.0008	79
20	19	37.5	6.3	3.2	0	0.0032	0.0009	72

solvent	Kerosene
solid	graphite
solvent viscosity	1.48 cp
solvent density	0.79 g/cm^3
solid density	2.25 g/cm^3
analyzer r.p.m.	500 rpm
analysis time	47 min

Figure 2 – Particle size distribution of feed from run number 12. It is assumed that the particles are composed of graphite.