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(57) Abstract

The invention concerns a process for the removal of volatile components from a feed stream including the steps of: (a) contacting one surface of a microporous hydrophobic membrane with the feed stream; (b) contacting the other surface of the membrane with a stripper stream which contains a redox reagent with which the volatile component will react; wherein the volatile component moves from the feed stream, passes through the membrane and reacts with the redox reagent in the stripper stream.

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PERSTRACTION WITH CHEMICAL REACTION

Field of the Invention

This invention relates to a membrane-moderated chemical process for the removal of dissolved oxygen from liquid or gas streams.

Background of the Invention

Boiler/turbine operation in power stations typically involves mechanical deaeration of water at two points; at the exhausted steam condenser using an extraction pump or steam jet ejector, and prior to entering the boiler using a spray or tray-type deaerator. Mechanical deaeration typically reduces dissolved oxygen levels to less than 1ppm.

However, even trace amounts of dissolved oxygen in boiler feedwater can cause severe oxygen pitting problems in the boiler tanks and hence complete removal is achieved by the addition of an oxygen scavenger at the storage section of the deaerator or at the feedwater storage tank. Indeed, some power stations do not have facilities for mechanical deaeration and rely heavily on chemical dosing.

The preferred oxygen scavenger is sodium sulfite. However, the current use of less effective and/or environmental unfriendly scavengers has resulted from the potential for thermal decomposition of sodium sulphite above 277°C to give hydrogen sulfide and sulfur dioxide. The degree of decomposition depends on pressure, concentration, pH and temperature. In general, direct dosing of water by sodium sulfite is limited to applications where operating pressures do not exceed 10300kPa (1500 psig) and other conditions are suitable.

Even under moderate pressures (up to 10300 kPa) some decomposition products are formed with resulting lowering of the pH of the steam and condensate through hydrogen sulfide and sulfur dioxide evolution. Acidic solutions act as corrosion catalysts. When condensate or water re-use streams are used as boiler feedwater, inhibition of the sulfite-oxygen reaction by chelants, organic contaminants in the feedwater, and other water treatment chemicals may also occur.

In boiler feedwater treatment, protection against corrosion during startup and shutdown and while the boiler system is on standby or in storage is important. These are critical periods since mechanical deaeration is not in operation. Corrosion during these stages occurs as the result of a large amount of cold water (where dissolved oxygen solubility is greatest) contacting the unit.

Cold water storage is normally accomplished using relatively high concentrations of chemicals, with or without forced circulation. However, these cause deposition problems when the unit is brought on line. For example, low pressure units typically use 200 ppm sodium sulfite with the resulting deposition of sulfate salts.

A membrane process for the removal of oxygen from water has been described by M.C. Yang and E. L. Cussler (AlChE J., 32 No.11, pp. 1910-1916, 1986) and by M.S.L. Tai, I. Chua, K. Li, W.J. Ng and W.K. Teo (Proc. "IMSTEC'92", Sydney, Australia, pp.306-308, 1992). In that process the water to be deoxygenated is pumped through the lumens of microporous, hydrophobic (non-wettable) hollow fibre membranes with a sweep gas (nitrogen) passing over the outside of the fibres (shell side) or vice versa. Oxygen desorbs from the water (feed) stream, diffuses across the membrane, and is then swept away by the gas stream. Yang and Cussler also employed a vacuum in place of the sweep gas with similar results. This process involves purely the "mechanical" removal of oxygen from the feed stream by the use of a "sweep" gas. No chemical reaction takes place at the membrane/sweep gas interface between the oxygen which has diffused through the membrane and the sweep gas. One disadvantage of this method is that oxygen, once having entered the stripper side of the membrane, must pass along the membrane face and thereby give a smaller oxygen partial pressure gradient than that which could be obtained if the oxygen was eliminated and accordingly the driving force of the oxygen removal is reduced.

Another related membrane process is that described by Z. Qi and E.L. Cussler (AlChE J., 31 No. 9, pp 1548-1553, 1985) and by M.J. Semmens, D.M. Foster and E.L. Cussler (J. Memb. Sci., 51, pp 127-140, 1990). In that process aqueous solutions of volatile solutes whose solubility can be enhanced by acid or base-induced ionisation are pumped over one face of a microporous, hydrophobic membrane, or through the lumens of hollow fibre membranes of that type, while a stripping solution containing 0.5 N sulfuric acid or 0.5 N sodium hydroxide contacts the opposite surface. The volatile solute desorbs from the feed stream, diffuses across the membrane, and dissolves in the stripping solution.

The above process is applicable to the removal of acidic and basic solutes only, that is, to solutes which produce H_3O^+ and OH^- ions respectively when dissolved in water. When the solute dissolves in the stripping solution the position of the equilibrium is pushed "to the right" by acid (basic solutes) or base (acidic solutes), thereby reducing the concentration of the solute in its original form. The partial pressure of that species at the stripper-membrane interface is thus reduced and hence an effective driving force is maintained. The following solutes were used in that work; bromine, hydrogen sulfide, iodine, sulfur dioxide, ammonia, ammonium sulfide, acetic acid, hydrogen chloride and lactic acid.

The equilibrium reactions discussed above are illustrated below for two acidic solutes, H_2S (hydrogen sulfide) and bromine (Br_2) which require a basic stripper (NaOH) and for a basic solute, NH_3 (ammonia) which requires an acidic stripper (H_2SO_4).

$$H_2S + H_2O \quad HS^- + H_3O^+$$

$$HS^- + H_2O \quad S^{2-} + H_3O^+$$

$$Br_2 + 2\,H_2O \quad Br^- + HOBr + H_3O^+$$

$$NH_3 + H_2O \quad NH_4^+ + OH^-$$

The process is not applicable to oxygen removal since oxygen does not react with water upon dissolution and is otherwise unaffected by the presence of acid or base.

Accordingly investigations have been carried out in an effort to improve the removal of oxygen from liquid and gaseous feed streams.

This invention is relevant to the removal of oxygen from boiler-feed and cooling stream water as treatment can take place in a low temperature, low pressure point in a Power Station such that decomposition products (with a resulting lowering of pH) are not formed. Further the invention is advantageous as the water stream does not make direct contact with the stripper so that reaction products eg SO_4^{2-} do not contribute to the "total solids content" of the water and hence scaling problems are reduced. The invention is also relevant to the production of ultrapure water for use in the semiconductor, pharmaceuticals and biotechnology industries since very low levels of oxygen can be achieved. This invention is thus applicable to any volatile solute which may be required to be removed from a solution or gas mixture such as the removal of oxygen from mixtures of gases. One such application is as a polishing step in the production of ultrapure nitrogen from air.

Description of the Invention

According to one aspect of the present invention there is provided a process for removing a volatile component from a first fluid containing.the volatile component including the steps of:

(a) contacting one surface of a microporous hydrophobic membrane with the first fluid;

(b) contacting the other surface of the membrane with a second fluid containing a redox reagent with which the volatile component will react,

whereby the volatile component moves from the first fluid, passes through the membrane and reacts with the redox reagent of the second fluid

Any gas-permeable hydrophobic membrane (non-wettable by water) in any structural configuration (hollow fibre, flat sheet, spiral wound, tubular, fan shaped etc) may be utilised. Examples include microporous polytetrafluoroethylene membranes such as those sold under the trade name Goretex, or polypropylene membranes such as those sold under the trade marks Celgard and Accurel.

Volatile components are those components which are capable of being oxidised or reduced by a redox reagent of the second fluid and include such components as oxygen, halogens and ozone which can be reduced; primary alcohols, aldehydes, ketones and alkenes which can be oxidised.

According to a preferred form of the invention the first fluid is an aqueous feed stream containing oxygen and the second fluid is a stripping solution containing an appropriate reducing agent for oxygen.

In another form of the invention the first fluid is a gaseous mixture containing oxygen. This process is identical to that described for the deoxygenation of liquids except that the oxygen is already in the gaseous form and therefore does not desorb form a liquid feed stream. That is, elimination of molecular oxygen from the stripper by reaction with a reducing agent causes molecular oxygen at the membrane-stripper interface to dissolve in the stripper and react. This oxygen is in turn replaced by oxygen which leaves the gaseous feed stream and passes through the membrane.

When the stripper solution is recirculated back to a stripper supply tank the stripper becomes saturated with the other gases present in the mixture and, unless these gases react with the reducing agent, will then not be removed from the gas feed stream.

A number of preferred types of reducing agents (oxygen scavengers) may be selected for use in this process. Oxygen scavengers which are in common use for boiler and cooling water treatment includes sodium sulfite (Na_2SO_3), sodium metabisulphite ($Na_2S_2O_5$), sodium bisulphite ($NaHSO_3$), hydrazine ($N_2H_4.H_2O$), hydroxylamine (NH_2OH) in the form of salts and alkyl derivatives, hydroquinone ($C_6H_4(OH)_2$) derivatives, and carbohydrazide ($NH_2NHCONHNH_2$). As an example, the oxygen scavenging action of sodium sulfite is indicated as follows:

$$2Na_2SO_3(aq) + O_2(aq) \quad 2Na_2SO_4(aq).$$

Preferably, the oxygen scavenger is non-volatile and does not produce volatile reaction products. Volatility will cause contamination of the feed stream from which the oxygen is being removed. For example, whilst the oxygen scavengers hydrazine and hydroxylamine and their homologs can be used in the process they are less effective than other reducing agents. Other reducing agents which may be used include stannous chloride ($SnCl_2$), cuprous chloride (CuCl), sodium borohydride ($NaBH_4$), tetramethylammonium borohydride ($(CH_3)_4NBH_4$) and pyrogallol ($C_6H_6O_3$).

Typically large concentrations of the oxygen scavenger may be utilised. Preferably Na_2SO_3 of 5-15 per cent w/v may be used so that the ratio of the volume of feed fluid to the volume of stripping solution is high.

For example, 500L of stripping solution containing 15 per cent w/v of sodium sulfite (75 kg total) will be sufficient to treat one megalitre of feedwater in a thermal power station, assuming that the initial oxygen content is 8 ppm. When it is considered that most of the feedwater is reused in the system with little reoxygenation, the volume ratio of the two streams is increased greatly; that is, the ratio of water volume to stripper volume is increased.

The preferred types of oxidants for volatile components which are capable of being oxidised include chromium trioxide, dichromate, chromic acid, permanganate, hydrogen peroxide, silver(I) oxide, Mn(VII) or Cr(VI).

In another preferred embodiment of the invention the temperature of the stripping solution may be increased by a few degrees, for example between 3 and 5^{o} C above the feed stream temperature. This may be desirable as water vapour pressure lowered by the downstream chemicals may otherwise cause dilution of the stripping solution by water vapour transport across the membrane.

The temperature range required for the effective removal of oxygen from liquids and gas mixtures using the membrane controlled process is limited by the temperature constraints of the membrane and reductants. The preferred temperature for the operation of the process is, however, between 0°C and 50°C.

The direction of the flow of these streams may be co-current or counter current, depending on the inter-facial pressure gradient requirements dictated by the design of the membrane module.

In the event that the second fluid (stripping solution) also initially includes oxygen the reducing agent completely depletes the stripping solution of oxygen so that the partial pressure of oxygen at the membrane-stripping solution interface is effectively maintained at zero.

This results in the creation of an oxygen partial pressure gradient from the feed stream (upstream) side to the stripping (downstream) side of the membrane with consequent diffusion of oxygen across the membrane. On contacting the stripping solution the oxygen dissolves and reacts with the reducing agent, thereby maintaining a partial pressure gradient. In this way the feed stream is stripped of oxygen.

Description of Drawings and Examples

The invention will now be further illustrated by reference to the drawings and examples in which:

Figure 1 is a schematic diagram of the process and equipment referred to in Example 1.

Figure 2 is a graph of oxygen mass transfer concentration (OMTC) or (Ko) verses feed flow rate for a stripper solution at three different flow rates.

Figure 3 is a graph of OMTC verses feed flowrate for three stripper solutions at constant stripper flow rate.

Figure 4 is a graph of OMTC verses feed flowrate for six stripper solutions at constant flow rate.

Figure 5 is a graph of OMTC verses feed Flowrate for an uncatalysed and catalysed stripper solutions at constant flow rates and at three different temperatures.

Figure 6 is a graph of Ko verses feed flow rate of the process described in Example 2.

Examples

The following are specific examples of preferred forms of the invention.

Example 1

In this example the operating conditions under which deoxygenation takes place were varied in order to characterise the process in terms of the various resistances to mass transfer. The conditions which were varied included feed (water) flowrate, stripper flowrate, stripper concentration, and reaction catalysis and temperature. The results of this work are applicable to the particular membrane module used, namely a Hoechst Celanese

Contractor, and may vary for other membranes and modules. The following specifications relate to the Hoechst module.

membrane type	hollow fiber isotactic polypropylene
membrane area	$0.4 m^2$
pore diameter	$0.05 \times 10^{-6} m$
porosity	30%

The feed stream employed in this example was distilled water saturated with oxygen. Oxygen-saturated feed was used to simulate the process by which oxygen would be extracted from feedwater for boilers dedicated to steam production for process use, that is where no prior mechanical deaeration is employed.

A schematic diagram of the process and equipment is shown in Fig. 1. The feedwater was pumped through the tube (lumen) side of the hollow fibers (shown as a single piece of membrane in cross-section in Fig. 1) before entering the base of a small cell where it immediately impinged on the membrane of a dissolved oxygen (DO) meter. The outlet stream was then discarded rather than being recirculated back to the feed reservoir in order that single-pass oxygen removal could be observed. A single pass was all that was required in this example as the purpose was to characterise the process in terms of its various resistances to mass transfer rather than to reduce the dissolved oxygen level to zero. The DO meter was regularly calibrated for zero ppm DO using the sulfite stripper in use at the time.

Sodium sulfite stripper solution was pumped through the shell side of the module with the outlet stream being returned to the stripper tank. In measurements requiring the catalysed sulfite-oxygen reaction an excess of cobalt (II) (as cobalt chloride) over that of a typical commercial product (3 parts Co^{2+}/10000 parts Na_2SO_3 by weight) was added to the stripper.

For measurements conducted at elevated temperatures the feedwater was maintained at 30°C and 40°C with stirring for approximately one hour prior to use to allow equilibrium to be established. Failure to observe this procedure results in air bubble formation in the module (supersaturation) and consequent errors in DO measurements. The stripper solution was heated to 30°C and 40°C immediately before taking each set of measurements.

Method

The method used to characterise the invention is described below.

The overall mass transfer coefficient (K_O or OMTC), that is the oxygen flux (removal) per unit driving force (oxygen concentration difference across the membrane) has four main components.

(a) feed side mass transfer

(b) stripper side mass transfer

(c) chemical reaction rate ($2SO^{2-}_3 + O_2 \rightarrow 2SO^{2-}_4$)

(d) membrane mass transfer

The method of this example was to determine which of the above resistances to mass transfer limits the process. The approach taken was to study the effects of varying the operating conditions of the process as already indicated.

Results

The following results and conclusions relate to the invention when operated as described above for Example 1.

Effect of feedwater and stripper flowrates on K_O (or OMTC)

The variations of K_O with feed flowrate using uncatalyzed 5% Na_2SO_3 at three stripper flowrates (50,200 and 400 mL/m) at 20°C are shown in Fig. 2. The horizontal trends of the K_O plots indicate that feed flowrate does not limit the process under the operating conditions employed. This is consistent with theoretical calculations which suggest that feed side resistance will not be limiting when K_O is less than 65-70 mg/m^{2}h ppm.

Figure 2 also shows that the K_O plots for the three stripper flowrates are not significantly different, suggesting that the operation of the invention is not limited by stripper side resistance.

Effect of stripper concentration on K_O

Figure 3 shows a plot of K_O versus feed flow rate for three different stripper concentrations (5,10 and 15% w/v) at a stripper flowrate of 200mL/m at 20°C. The results show that K_O decreases with increasing stripper concentration over the range of concentrations studied. These results indicate that the operation of the invention is sensitive to stripper concentration, presumably because of reduced solubility and slower diffusion of oxygen in the more concentrated solutions.

Effect of catalysis of the sulfite-oxygen reaction on K_O

The variation of K_O with feed flowrate for the three stripper concentrations at 200mL/m at 20°C with and without catalysis is shown in Figure 4. The results show that catalysis has a marked effect on mass transfer, as summarised below.

Na_2SO_3 concentration % w/v	average K_O (or OMTC) (uncatalysed) mg/m^{2}h ppm	average K_O(or OMTC) (catalysed) mg/m^{2}h ppm
5	23.5	47.2
10	14.6	43.6
15	11.4	42.9

Of particular interest is the similarity of the average K_O values for each stripper concentration when the reaction is catalysed. This suggests that the process is not limited significantly by stripper concentration when the reaction is catalysed. This is attributed to a shorter diffusional path for oxygen before colliding with a sulfite ion with appropriate kinetic energy to overcome the now lowered activation energy.

The efficiency of the process depends on the magnitude of K_O. This is increased by catalysis. Catalysts which can be used include inorganic salts of cobalt, cobalt complexes, manganous salts, manganous complexes, hydrogen peroxide, chlorite, a variety of transition metal ions (Co^{2+}, Mn^{2+}, Cu^{2+}) and light.

Effect of temperature on K_O

The variation of K_O with feed flowrate using uncatalysed and catalysed 10% w/v Na_2SO_3 stripper at 400mL/m at 20,30 and 40°C (each ± 2°C) is shown in Figure 5. The use of elevated temperatures had a marked influence on K_O, with both the uncatalysed and catalysed values being increased by approximately 100% on raising the temperature from 20 to 40°C. The average K_O values at each temperatures are summarised below.

Temperature (°C)	average K_o uncatalysed (mg/m^{2}h ppm)	average K_o catalysed (mg/m^{2}h ppm)
20	20.1	33.9
30	22.4	61.0
40	39.2	71.4

The fact that the K_o increased sharply with temperature confirms that the process is limited by reaction rate. There is nothing in the feed side and membrane mass transfer mechanisms that can explain such a sensitivity to temperature. On the other hand, reaction rates are strongly dependent on temperature and are expected to approximately double for each 10° C rise. This suggests that further increases in temperature can result in substantially higher fluxes. The fact that the increase in K_o from 30 to 40°C was only 20% indicates that another resistance, probably feed side mass transfer, is starting to limit the process at high fluxes as predicted on theoretical grounds.

Membrane mass transfer

In the absence of an independent measurement of the membrane mass transfer coefficient, the value has been estimated from theory. The most applicable gas permeation theory is Knudsen diffusion. The membrane mass transfer coefficient estimated from this theory is of the order of 10^7 mg/m^{2}h ppm, which is several orders of magnitude higher than the measured overall mass transfer coefficients. This strongly suggests that the membrane resistance is insignificant.

Example 1 serves to demonstrate the characteristics of the invention when used in conjunction with a Hoechst Celanese Contactor. These characteristics are summarised below.

(1) Feed side mass transfer resistance is not limiting at low fluxes. Results obtained at elevated temperatures suggest that it may be limiting when the K_o increases to about 70 mg/m^{2}h ppm in accordance with theoretical predictions.

(2) Stripper side mass transfer is not limited by flowrate but is limited by high stripper concentration. However, the latter has an insignificant effect when the sulfite-oxygen reaction is catalysed.

(3) The process is limited by the rate of the sulfite-oxygen reaction. However, K_O can be at least doubled by catalysis.

(4) An approximately 100% increase in K_O can be achieved for both the uncatalyzed and catalysed process by stripping at 40°C rather than at ambient temperature (20° C).

Example 2

This example was intended to confirm the best performance achieved in Example 1, namely a K_O of 70-75 mg/m^{2}h ppm using catalysis at 40°C. In this case however the feedwater DO content was adjusted to about 1 ppm by the addition of a small quantity of Na_2SO_3 in order to stimulate a process in which prior mechanical deaeration had been effected, for example that in a thermal power station.

A Hoechst Celanese contractor identical to that used in Example 1 and having no previous use was employed in this example. The stripper solution used was 5% w/v Na_2SO_3. All other experimental details are as given in Example 1.

Results

A plot of K_O versus feed flowrate is shown in Fig. 6. Unlike the data obtained in Example 1 (Fig. 5), K_O shows a definite increase with increasing flowrate before appearing to level out at 80-85 mg/m^{2}h ppm. This value is in reasonable agreement with that obtained in Example 1 and is accepted as confirmation of the former results. Indeed, the small discrepancy between the values may be attributed to the use of different modules with different membrane histories.

In Example 1, K_O remained constant over the range of feed flowrates used and it was therefore concluded that feedside resistance is non-limiting, at least at lower fluxes. In this example however, feedside resistance is indeed limiting at even low fluxes. This observation is attributed to the low DO level of the feedwater. It appears that DO depletion of the feedwater in the module is so rapid due to its low initial level that the amount of oxygen transported across the membrane is dependent on the rate of delivery to the module.

Based on the results discussed in Example 2 the following can be concluded.

(1) The best performance achieved in Example 1 has been confirmed in an independent trial.

(2) The invention is equally suited to oxygen removal from saturated and low concentration streams although relatively high feed flowrates are required in the latter case to reduce feed side resistance.

Example 3

In this example the effectiveness of the invention in producing very low levels of oxygen in the feed stream by recirculation through a single Hoechst Celanese Contractor was tested. The latter was identical to those used in Examples 1 and 2 but with a different membrane history.

A sample of 1000mL of tap water which was saturated with air was pumped through the lumens of the hollow fiber module with recirculation back to the feed reservoir at 23°C. A 5% w/v Na_2SO_3 solution was pumped through the shell side of the module with recirculation back to the stripper tank. The flowrate of each stream was 1000 mL/m. In this example the water feed was protected from reoxygenation by a blanket of carbon dioxide. The DO meter was placed in the feed tank which was stirred by the returning oxygen-depleted feed.

Results

The following results were obtained.

Pumping time (s)	**DO content (ppm)**
0	7.05
60	0.74
120	0.00

These results demonstrate that very low DO levels can be obtained using the invention. It should be pointed out however that the DO meter used in this work could be read to the nearest 10 parts per billion only and hence a trace amount of oxygen probably remained after 120 seconds.

Example 4

The work described in this example was carried out to demonstrate that the invention is not limited to use in conjunction with the Hoechst membrane and/or module.

A sample of 500ml of distilled, deionised water was pumped over one face of a flat sheet Gortex polytetrafluoroethylene (PTFE) membrane (pore diameter 0.2 micron, surface area $0.0155m^2$) while a stripping solution containing 5 per cent w/v sodium sulfite and 0.08 per cent w/v sodium hydroxide was pumped over the opposite face. A plate and frame test cell was used for this purpose.

Both streams were recirculated back to their respective feed containers at a rate of 450ml per minute. The distilled water, which had previously been allowed to become saturated with oxygen and carbon dioxide, was protected from further solubilisation of these gases by a blanket of nitrogen gas. The temperatures of the water and stripper solutions were 23° C and 25°C respectively. Using a dissolved oxygen meter and pH meter for monitoring the water stream the following results were obtained.

Pumping time (sec)	**Dissolved oxygen content (ppm)**
0	9.90
30	2.74 initial pH 5.25
45	0.73
60	0.18 final pH 6.66
75	0.07
90	0.03
100	0.00

These results show that dissolved oxygen can be removed from the said stripping solution rapidly using the Goretex membrane.

Example 5

This example demonstrates the effectiveness of the invention in the removal of oxygen from gas mixtures. The particular application chosen for this experiment was the removal of oxygen from air.

Air was pumped through the lumens of a Terumo Capiox 350 hollow fiber module (polypropylene membrane, area $5m^2$) at various flowrates in the range of 320 to 1160 mL/m. The stripper solution (5% w/v Na_2SO_3) was pumped through the shell side of the module in concurrent flow. The gas exiting the module was sampled and analysed by a Fisher Gas Partitioner (Model 1200) with a thermal conductivity detector and a column temperature of 45°C. A double headed peristaltic pump was used to cater for both the air and stripper streams and hence the volumetric stripper flowrate relating to each sample is equal to that of air. The experiment was conducted at 21°C.

Results

The following results were obtained.

Air/stripper flowrate (mL/m)	**oxygen content after single pass (%)**
320	5.8
550	9.5
660	9.9
810	11.8
910	13.5
1050	14.3
1160	14.9
untreated air	20.7

The results demonstrate that the invention is effective in the removal of oxygen from air.

This invention provides a means for removing oxygen from liquids in which it is dissolved or from gas mixtures by transport across a micro porous, hydrophobic membrane to a stripping solution of an appropriate reducing agent such as sodium sulfite. The oxygen is converted to a new chemical species by reaction with the reducing agent so that the partial pressure of oxygen at the membrane-stripper interface is effectively maintained at zero. The resulting steep partial pressure gradient provides a driving force which is capable of reducing the dissolved oxygen content in the feed stream to very low levels.

CLAIMS

1. A process for the removal of a volatile component from a first fluid containing the volatile component including the steps of :

   (a) contacting one surface of a microporous hydrophobic membrane with the first fluid;

   (b) contacting the other surface of the membrane with a second fluid containing a redox reagent with which the volatile component will react,

   whereby the volatile component moves from the first fluid, passes through the membrane and reacts with the redox reagent of the second fluid.

2. A process according to claim 1 wherein the redox reagent is a reductant.

3. A process according to claim 2 wherein the reductant is selected from a group including sodium sulfite (Na_2SO_3), sodium metabisulphite ($Na_2S_2O_5$), sodium bisulphite ($NaHSO_3$), hydrazine ($N_2H_4.H_2O$), hydroxylamine (NH_2OH) in the form of salts and alkyl derivatives, hydroquinone ($C_6H_4(OH)_2$) derivatives, carbohydrazide ($NH_2NHCONHNH_2$), stannous chloride ($SnCl_2$), cuprous chloride (CuCl), sodium borohydride ($NaBH_4$), tetramethylammonium borohydride ($(CH_3)_4NBH_4$) and pyrogallol ($C_6H_6O_3$).

4. A process according to claim 1 wherein the redox reagent is an oxidant.

5. A process according to claim 4 wherein the oxidant is selected from a group including chromium trioxide, dichromate, chromic acid, permanganate, hydrogen peroxide, silver(I) oxide, Mn(VII) or Cr(VI).

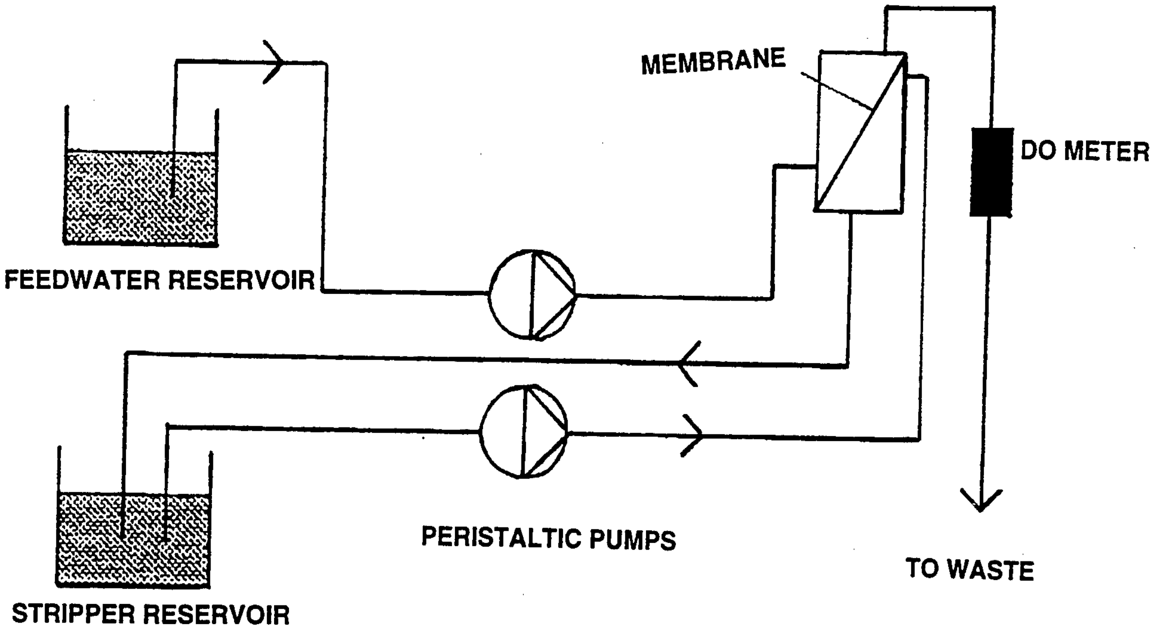
6. A process according to claims 2 or 3 wherein the volatile component is oxygen.

7. A process according to any one of the preceding claims wherein the first fluid is a gas mixture.

8. A process according to any one of the preceding claims wherein the temperature of second fluid exceeds that of the first fluid.

9. A process according to any one of the preceding claims wherein the temperature of the second fluid is maintained at or above the first fluid.

10. A process according to any one of the claims substantially as hereinbefore described by reference to the examples.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PERISTALTIC PUMPS
TO WASTE

Figure 1

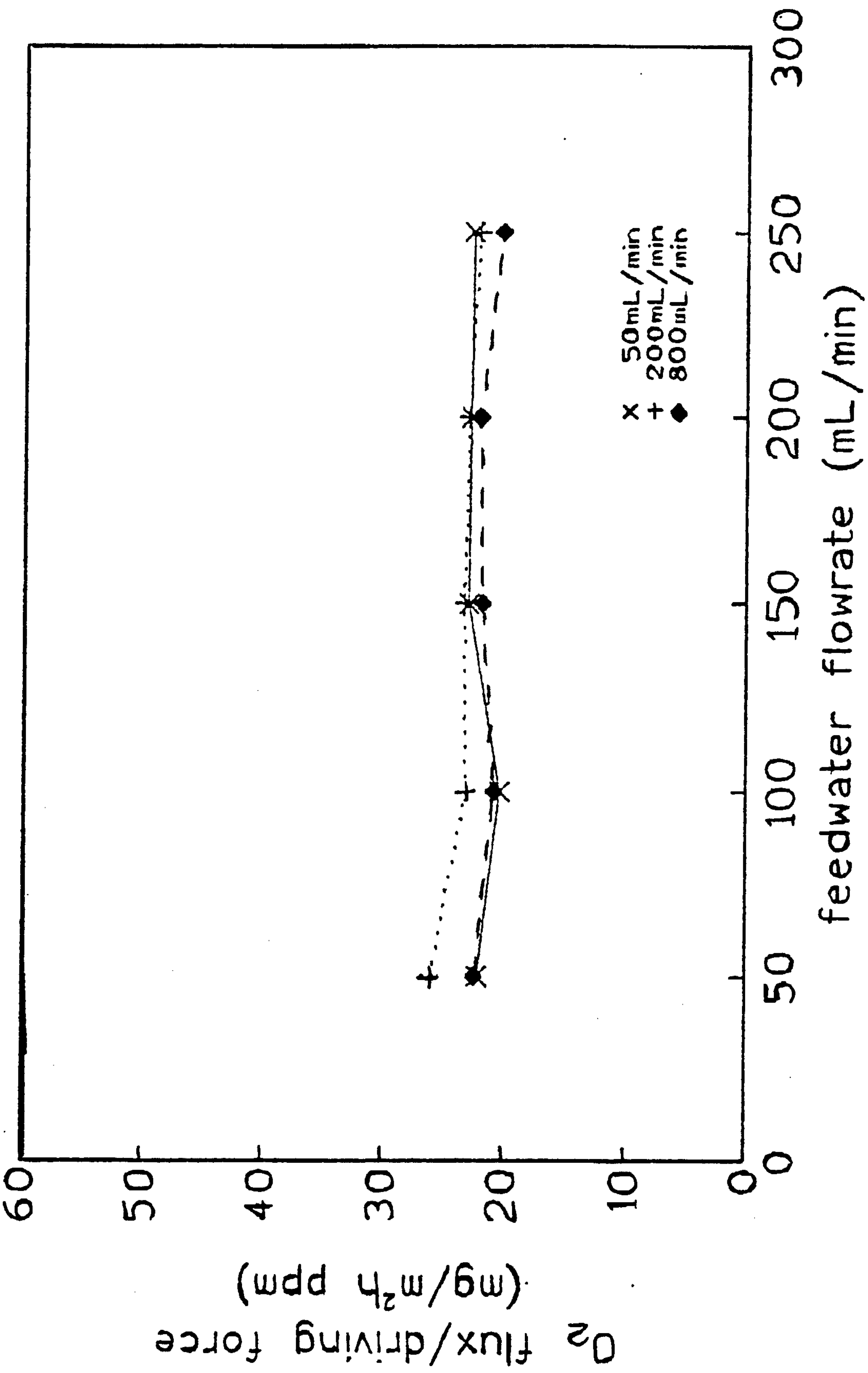
60
50
40
30
20
10
0
O_2 flux/driving force
(mg/m^2h ppm)
0
50
100
150
200
250
300
feedwater flowrate (mL/min)
× 50mL/min
+ 200mL/min
◆ 800mL/min

Figure 2

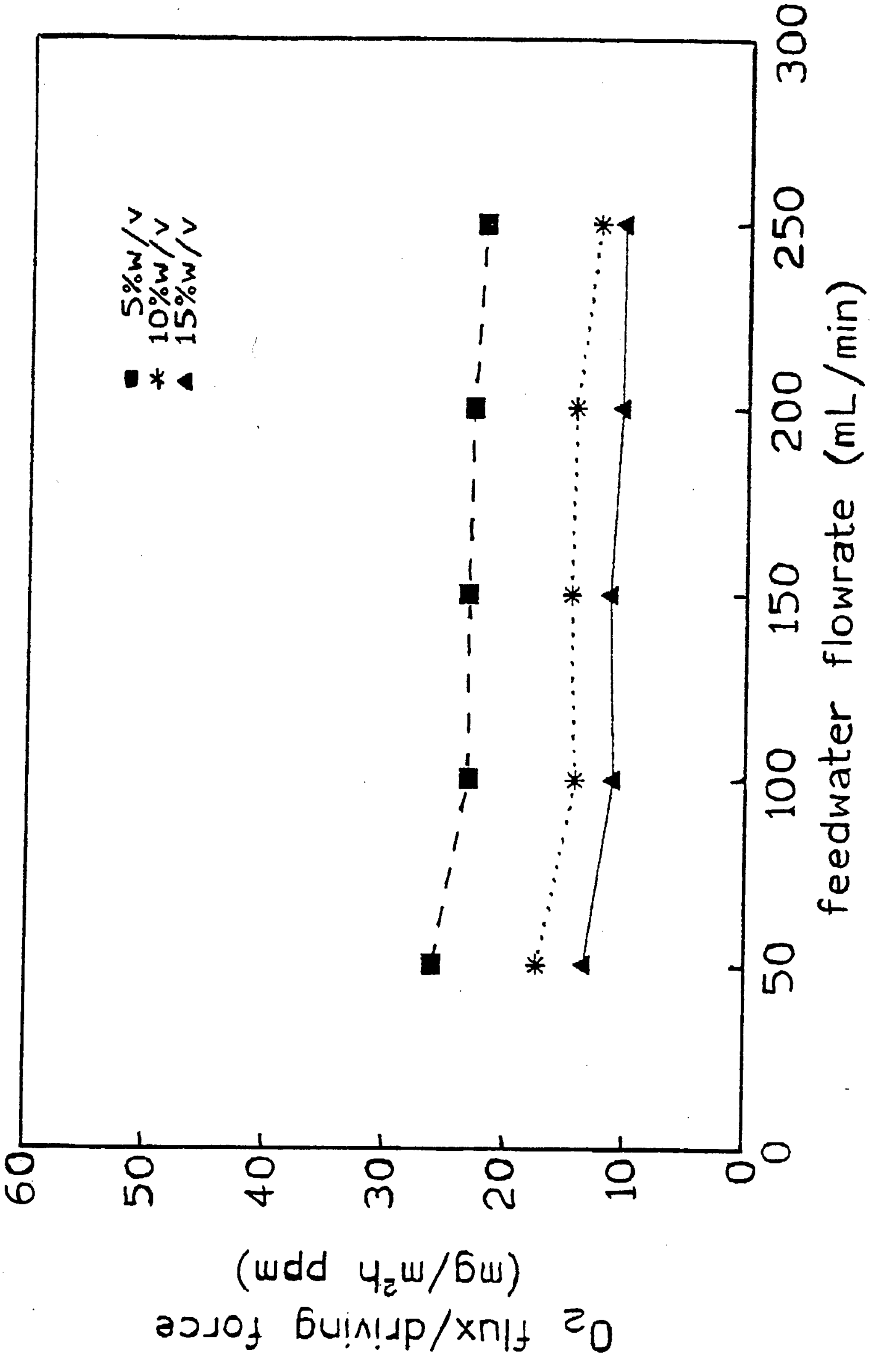
5%w/v
10%w/v
15%w/v
0
50
100
150
200
250
300
feedwater flowrate (mL/min)
0
10
20
30
40
50
60
O_2 flux/driving force
(mg/m^{2}h ppm)

Figure 3

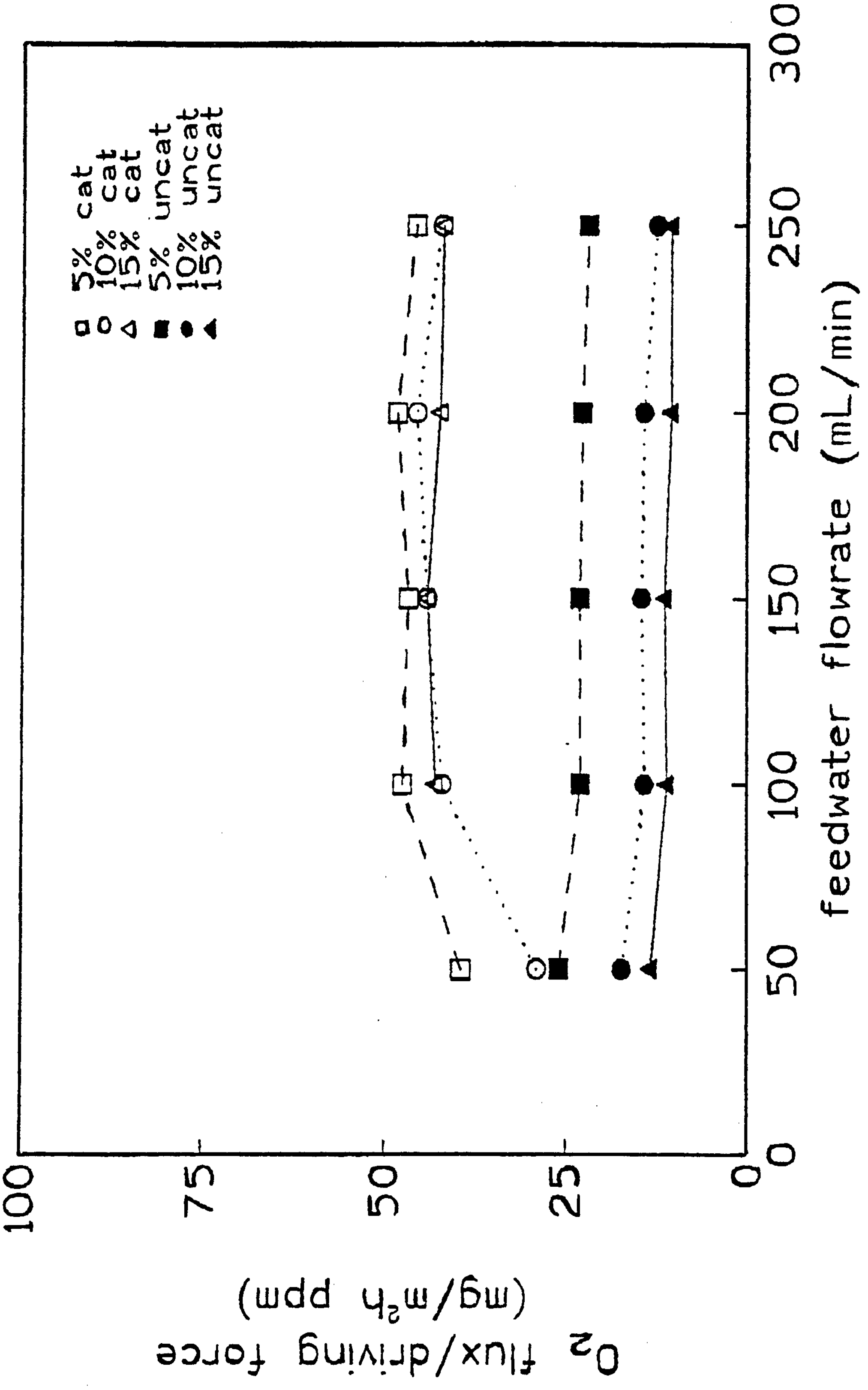
O_2 flux/driving force (mg/m^{2}h ppm)
0
25
50
75
100
0
50
100
150
200
250
300
feedwater flowrate (mL/min)
□ 5% cat
○ 10% cat
△ 15% cat
■ 5% uncat
● 10% uncat
▲ 15% uncat

Figure 4

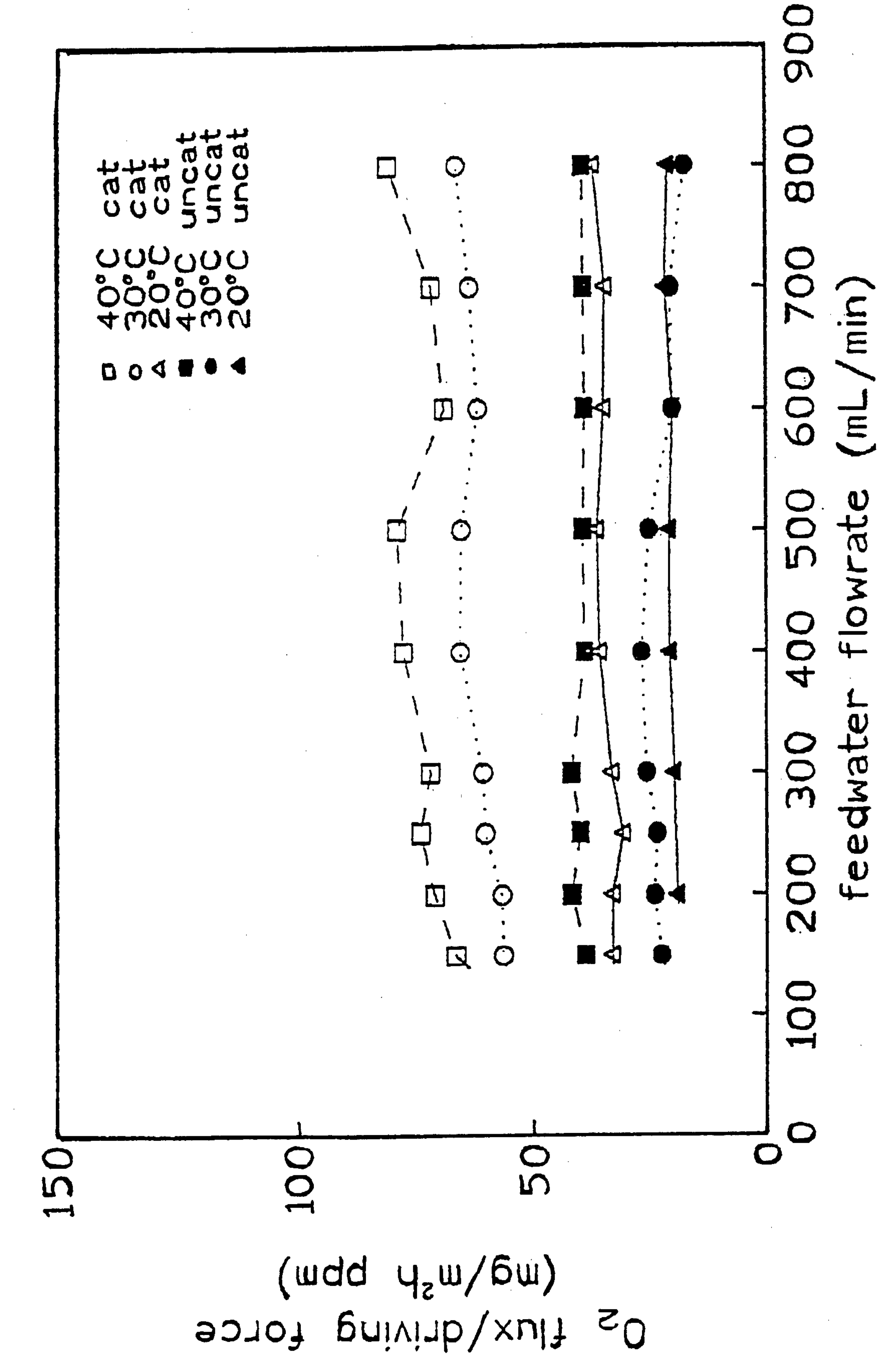
□ 40°C cat
○ 30°C cat
△ 20°C cat
■ 40°C uncat
● 30°C uncat
▲ 20°C uncat
O_2 flux/driving force (mg/m^{2}h ppm)
0
50
100
150
feedwater flowrate (mL/min)
0
100
200
300
400
500
600
700
800
900

Figure 5

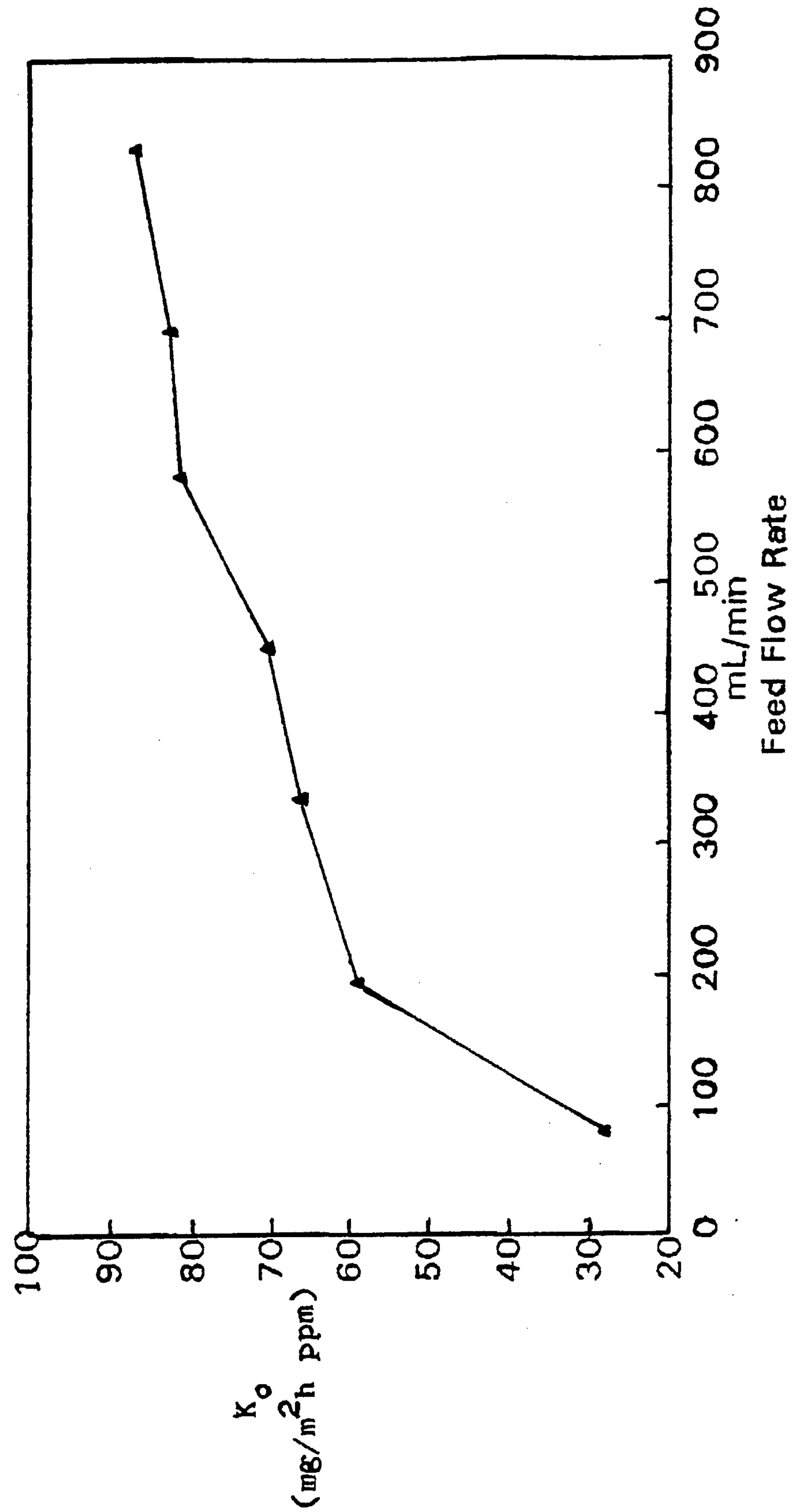
K_o
(mg/m^{2}h ppm)
100
90
80
70
60
50
40
30
20
0
100
200
300
400
500
600
700
800
900
mL/min
Feed Flow Rate

Figure 6

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU 94/00038

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl.^{5} B01D 61/36

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC^5 B01D 61/36
IPC^4 B01D 13/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
AU : as above

Electronic data base consulted during the international search (name of data base, and where practicable, search terms used)
DERWENT

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	US,A, 4729773 (KOZO et al) 8 March 1988 (08.03.88)	
A	US,A, 4758416 (HOWARD et al) 19 July 1988 (19.07.88)	
A	US,A, 4929357 (SCHUCKER) 29 May 1990 (29.05.90)	
A	US,A, 4962271 (BLACK et al) 9 October 1990 (09.10.90)	

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier document but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search 11 May 1994 (11.05.94)	Date of mailing of the international search report 16 May 1994 (16.05.94)
Name and mailing address of the ISA/AU AUSTRALIAN INDUSTRIAL PROPERTY ORGANISATION PO BOX 200 WODEN ACT 2606 AUSTRALIA Facsimile No. 06 2853929	Authorized officer **B. BOURKE** B Bourke Telephone No. (06) 2832148

INTERNATIONAL SEARCH REPORT

Information on patent family membe

International application No.
PCT/AU 94/00038

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report	Patent Family Member		
US 4729773	JP 62204086		
US 4758416	AU 82664/87	BR 8707124	CA 1296866
	DK 6874/87	EP 279085	IN 170514
	JP 63197514	NO 875460	US 4741888
	ZA 8709594		
US 4929357	CA 2020696	EP 416752	JP 3077634
	US 4983338	US 5075006	
US 4962271	CA 2031163	EP 434342	JP 4110393
			END OF ANNEX