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(57) Abstract

A method is proposed to recover and concentrate perfluorinated compounds and hydrofluorocarbon gases from effluent gases in manufacturing processes. The method involves contacting the gas with a membrane module equipped with inorganic, molecular sieve membranes and applying a pressure difference across the membrane by compressing the feed gas or applying a vacuum to the permeate or both. The PFC and HFC gases are retained to a very high degree, achieving higher concentrations of PFC and HFC components while reducing the size of or eliminating the need for complementary processes to scavenge the PFC and HFC gases that would otherwise pass through the membrane to the permeate side.

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Recovery of perfluorinated compounds and hydrofluorocarbon gases using molecular sieve membranes

Field of the Invention

This invention relates to a method for recovering or concentrating perfluorinated compounds (PFC) and hydrofluorocarbon (HFC) gases from effluent gases in manufacturing processes.

Background of the Invention

There are many manufacturing processes today that make use of perfluorinated compounds (e.g., NF_3, SF_6, WF_6, CF_4), and hydrofluorocarbons (e.g. CHF_3). These include such processes as cathode ray tuber (CRT) manufacture, aluminum foundries, refrigerants, VLSI circuit cleaning and semiconductor manufacture (dry etch). While these gases tend to be fairly inert, they do present a significant danger to further global warming by the greenhouse effect because of their extremely long lifetimes and their high IR absorbance capacity. This illustrates in the following Table 1 (see SEMATECH, Technology Transfer, Global warming: A White Paper on the Science, Policies, and Control Technologies that impact on the U.S. Semiconductor Industry, 3/20/94).

Table 1 - Global warming potentials for industrial chemicals.

Chemical	Lifetime (years)	GWP (100 years)
CF_4	>50,000	10,900
C_2F_6	>10,000	11,500
NF_3	<179	24,200
SF_6	3,200	21,000
C_3F_8	>10,000	N/A
CO_2	120	1
CH_4	10.5	11
CFC-11	55	3,400
CFC-12	116	7,100
N_2O	132	270

Because of envisioned restrictions on use of polyfluorinated compounds (PFCs) and the voluntary commitment of semiconductor manufacturers to restrict PFC emissions, PFC costs will increase and the pressure to recover the PFC from process waste streams will increase.

The techniques presently used for PFC removal from waste streams include scrubbers (e.g. of Ecosys, ATMI) and scrubbers combined with cryogenic distillation (Praxair US 5,502,969) and permeation and condensation by means of glassy membranes(EPA 0 754 487). The use of scrubbers has the drawback that the scrubbed liquor must be treated and/or the PFC's safely incinerated without benefit of the recovered PFC's. The scrubber and distillation process has the advantage of recycling but the PFC must be separated from the scrubbing liquid and proper disposal of the scrubber liquid must still be dealt with.

EPA 0 754 487 discloses a process for the separation and recovery of perfluorocompound gases by means of glassy polymeric membranes. Such membranes, however, are not selective enough to completely retain all of the PFC and HFC compounds concerned. As a result more downstream processing of the PFC and HFC compounds that have escaped to the permeate is required either by scrubbing or by absorbers. This limitation of selectivity results in a limit to the volume concentration that the feed stream can be subjected to, which leads to a relatively high amount of non-condensable carrier gas (e.g. nitrogen) still being in the non-permeate (reject) stream. As a result higher pressures and temperatures would be required to reach the desirable extent of recovery of PFC's by condensation.

An example of this limitation is shown in Example 1 of the cited EPA 0 754 487. In the following Table 2 are shown the extent of PFC and HFC losses to permeate of an effluent stream which has been concentrated 15 fold.

As can be seen in the table, while the concentration of the CF_4 in the permeate stream is about 1% of its concentration in the feed stream, , that of the C_2F_6 is almost 2% and that of the CHF_3 is over 40%.

Table 2 - Data of Example 1 of EPA 0 754 487

Compound	Stream	Feed	Permeate	Retentate	% Lost to permeate
		Conc. (Vol%)			
CF_4		1.10%	0.01%	18.15%	0.85%
C_2F_6		0.95%	0.02%	15.66%	1.97%
CHF_3		1.03%	0.48%	9.54%	43.70%
Volume(lt)		193	181	12	
Pin(bara)	5.44 bara				
Pperm(bara)	0.066				
		Pressure ratio	82.7	Volume conc. Ratio	15.1

It should be noted that, in said Example, as a result of a volume concentration ratio of only 15, the retentate stream still contains 56% nitrogen, and the resulting partial pressures of the PFC's are accordingly lower than they would otherwise be. By using the Weller-Steiner equation - see e.g. Pettersen and Lien, Gas Separation and Purification, 9,. pp. 151-169 (1995) - and back-calculating the overall selectivity of the membrane based on the concentration of nitrogen in the permeate, the selectivity of the membrane for nitrogen over the mixture of PFC's in the feed stream is only 41.

It has been shown in the literature that some glassy polymers have a tendency to swell when exposed to organics, and the larger the organic molecule the greater the tendency for swelling (see J. of Memb. Sci.). This is shown in the above example by the fact that C_2F_6 is more poorly retained than CF_4 even though C_2F_6 is a larger molecule. As the cited EPA states: "It has been suggested in the prior art that the intrinsic permeability of a polymer membrane is a combination of gas diffusion through the membrane, controlled in part by the packing and molecular free volume of the material, and gas solubility within the material"

Examples 3 of the cited EPA gives a further example of the problem. In the membrane separation step, over 10% of the NF_3 and over 20% of the CHF_3 is passed to the permeate even though the feed is only concentrated somewhat less than threefold.

In addition, it is well known that glassy polymeric membranes have a drastic flux drop as their operation temperature is reduced.

A specific PFC to which this invention refers, is sulfur hexafluoride (SF_6). SF_6 is a very inert gas that is finding increasing use in the electrical power industry, magnesium and aluminum foundries, and semiconductor manufacture (see E. Cook, "Lifetime Commitments: Why Climate Policy-makers Can't Afford to Overlook Fully-Fluorinated Compounds," World Resources Institute, Washington D.C, 1995 cited in Christophoru, L.G. and R.J. Van Brunt, IEEE Trans. Dielectrics and Electric Insulation, 2(5), pp. 952-991 (1995). Its dielectric properties make it three times as resistant as air to electric breakdown. As a result 80% of SF_6 is used in blanketing electrical installations, such as circuit breakers and switching stations. Its inertness, combined with the ability to provide fluorine atoms, makes it attractive to both the semiconductor industry, where it is used in reactive ion etching (RIE) and in post-etching treatments (PET) of integrated semiconductor circuits, and to the magnesium and aluminum foundries. In electronics applications it is found in mixtures with Ar or 0_2 and in the foundry applications it can be found mixed with air. The estimated SF_6 production in 1993 was 7000 metric tons/year and it is expected to reach 10,000 metric tons/year by 2010 (see the above publication by E. Cook). The increased demand in the semiconductor industry is resulting in potential shortages and increasing price for this gas.

SF_6 has extremely strong IR adsorption bands at 522 and 345 cm^{-1} and additional bands at wave numbers of 947, 770, 640, and 615 cm^{-1} (Matheson, Handbook of Gases, "The Matheson Unabridged Gas Data Book - A compilation of physical and thermodynamic properties", 5th Ed., 4 Vols. (1974) published by Matheson Gas Company). As a result it is an extremely potent greenhouse gas, viz. a gas that absorbs IR radiation emitted by the earth's surface, especially in wavelengths between 7-13 um. In fact, it is 25,000 times more effective as a greenhouse gas than $C0_2$ and, because of its chemical inertness, its atmospheric lifetime is estimated to be 800-3200 years(see the above publication by Christophorou and Brunt). For all practical purposes whatever SF_6 released into the atmosphere will remain there within the foreseeable future and continue to accumulate and contribute to the greenhouse effect. As a result, there will be an increasing need to curtail SF_6 emissions, if this cumulative effect is not to cause irreversible harm to earth's climate. Continued use of SF_6 for industrial purposes will require abatement and re-design of processes to afford recycling the SF_6 or reducing the amount used.

Recycling, requires separation of the SF_6 from the other gases with which it has been diluted as a result of leakage out of its container or from other gases drawn in with the SF_6 into the duct system which collects the process waste gas.

SF_6 is a condensable gas and liquefies at room temperature at 23 atmospheres. Its vapor pressure diagram is provided in Fig. 7 (based on data from the above cited Matheson, Gas Handbook). As such, it could be conceivably condensed from a mixture of non-condensing gases (e.g. air, argon, etc.). However, if mixed with $C0_2$ it would be hard differentially to condense it and a cryogenic distillation system would be required for this purpose. In cases where the concentration of SF_6 is low (e.g. < 10%), cryogenic condensation is not practical because of the low SF_6 partial pressure, which makes it impossible to recover significant amounts of SF_6 without operating at liquid nitrogen temperatures or lower. Even when the waste stream is fairly concentrated in SF_6 (e.g. > 30%), fairly complete removal (>90%) from the waste stream requires that the gas mixture be compressed to at least 5 bara and cooled to at least -75° C. This is illustrated in Fig. 8. Carrying out such a recovery would require a fairly large recovery unit with significant refrigeration duties, which could not be easily distributed among different processing units or duct sites in a manufacturing facility. Further, the compressors needed for large gas flows would be quite large. Therefore that the art does not provide a satisfactory process for separating and recovering SF_6 from a mixture of gases, particularly from waste gas streams which are an outlet of industrial processes.

It is the purpose of this invention to suggest a more efficient recovery or concentration process for PFC's, based on the use of non-polymeric, molecular sieve membranes. Such membranes have extremely high selectivities for molecules whose size exceeds the pore size of the molecular sieve membrane material; and, additionally, have a relatively small loss of flux as the temperature is reduced allowing it to be used at reduced temperatures further to enhance selectivity (see EPA 0 621 071), whereby process advantages are achieved by operating the membrane at temperatures close to those of the condenser.

Molecular sieve membranes are defined in Way and Roberts (Separation Science and Technology, 27(1), 1992, p. 35) "Molecular sieving refers, in its most absolute sense, to the complete blocking of transport of a certain size or shape of molecule and the free passage of smaller or differently shaped molecules." This reference cites materials such as zeolites and molecular sieve carbon as materials that exhibit said behavior or elements of said behavior.

There are numerous literature reports of membranes made from said materials (see Koros, CEP, October, 1995) especially from microporous (having pore size less than 2 nm, as defined by IUPAC convention) inorganic materials such as amorphous glassy carbon (Koresh and Soffer, Sep. Sci. and Technology, 18 (1983) p273; Jones and Koros, Carbon, 32, (1994), ;1419) crystalline ceramic membranes such as zeolites (Petersen, J, et al. "Ceramic Zeolite Composite Membranes for Gas Separation " at 1993 International Congress on Membranes and Membrane Processes (ICOM '93)), porous, amorphous glass membranes (Ma, Y. et al. "Gas Separation by Use of Microporous Inorganic Membranes", poster presented at ICOM '93, Heidelberg, Germany). A microporous membrane will act as a molecular sieve when the effective smallest dimension of its pores lies between that of the molecules to be permeated and that of the larger molecules to be retained. A molecule retained by a molecular sieving membrane still have a positive energy of activation for diffusion across the membrane which is significantly higher than that of the molecules which are passed by the membrane. The nature of the molecular sieving membranes is such that the selectivities tend to be very high relative to polymer membranes as can be seen from the selectivities found in the cited references.

It is another purpose of this invention to provide such a process which does not require the use of very high pressures or of very low temperatures.

It is a further purpose of this invention to provide such a process which permits to recover at least 80%, and preferably 90% or more, of the PFC or HFC's, particularly of SF_6, contained in the process gas mixture.

It is a still further purpose of this invention to provide such a process which permits to obtain the PFC or HFC's, particularly SF_6, with a concentration or purity equal to or exceeding that of the composition of the feed stream to which the recovered SF_6 is to be returned.

It is a still further purpose of this invention to provide such a process which permits to separate the PFC or HFC's in a single step.

It is a still further purpose of this invention to provide such a process which permits to separate the PFC or HFC's from nitrogen, oxygen, argon and in general, non-compressible gases, or gases with which it can co-condense, e.g. CO_2.

It is a still further purpose of this invention to provide such a process which permits to recover SF_6 from waste gas streams which are the outlet of Mg and Al foundries, casting and production industries, from releases in electric power installations during operation or maintenance, and from the electronics industry in which SF_6 serves as a reactant.

It is a still further purpose of this invention to provide device and apparatus means for carrying out the process of the invention.

Other purposes and advantages will appear as the description proceeds.

Summary of the Invention

The process for the separation and recovery or concentration of perfluorinated compounds, hereinafter PFC's (e.g. SF_6, NF_3, WF_6, CF_4, C_2F_6 etc.) and hydrofluorocarbons, hereinafter HFC's (CHF_3 etc.), from gaseous effluent streams of manufacturing processes which contain one or more PFC or HFC, according to the invention, comprises the steps of:

a) bringing the gaseous effluent stream into contact with a membrane module at a first pressure, hereinafter "high pressure";

b) drawing the permeate, viz. the gas that has passed through the membrane, in such a way as to maintain a second pressure, hereinafter "low pressure', lower than the high pressure, on the other side - the permeate side - of the module; and

c) recovering the retentate, viz. the gas that has not passed through the membrane, having an enriched concentration of the PFC or HFC molecules relative to the feed stream;

characterized in that the membrane is a molecular sieve membrane which passes nitrogen but not PFC and HFC molecules, and has a retentivity ratio of the PFC or HFC over nitrogen that is at least 50, and preferably 300, and a permeance for nitrogen that is at least 80 SL/m^2-hr-bar (standard liters per square meter per hour per bar), and preferably at least 200 SL/m^2-hr-bar, provided that if the PFC or HFC has a molecular diameter equal to or smaller than that of CHF_3 , the permeance for N_2 should be at least 50 SL/m^2-hr-bar.

The molecular sieve membranes which have the aforesaid, required retentivity ratio and permeance are chosen from among inorganic, microporous, molecular sieve membranes.

Since the gases of interest in this invention are required to be retained instead of being passed by the membrane, it is found convenient to define the retentivity of the membrane as the reciprocal of the permeance of the gas, and the retentivity ratio is the retentivity of the PFC or HFC gas divided by the retentivity of the non-condensable gas with which it is mixed. Therefore, the lower the permeance of a gas, the higher its retentivity. By analogy, the retention ratio of a membrane will be the ratio of the retentivity of the slowest gas to the other gases in the processed mixture. Said retentivity ratio is equal to the permselectivity, which is the ratio of the permeance of the more permeable non-condensing gas to that of the less permeable (PFC or HFC) gases. By "non-condensable gases" are meant gases whose critical temperature is lower than 0°C.

The molecular sieve membranes preferably have a pore size larger than the effective molecular diameter of the non-condensable gases mixed with the PFC or HFC's in the industrial exhaust effluent gas to be treated, but smaller than the effective molecular diameters of the PFC and HFC's. Since the most common non-condensable gas is nitrogen, the membrane should have a pore size of at least 3.7 Angstrom. Should the gas stream to be treated contain, in place of nitrogen, another non-condensable gas having a larger effective molecular diameter, the minimum pore size of the membrane should be proportionally higher to permit said gas to pass through the membrane. Since the maximum pore size must be such as to retain the PFC or HFC's which it is wished to recover, it must not exceed the molecular diameter of the PFC or HFC and may vary depending on said diameter. In most cases, it would not be higher than 5.5 Angstrom.

The gases with which the PFC or HFC's are usually diluted are permanent gases found in air (O_2, N_2, Ar) and gases used in certain industrial processes (O_2, Ar, CO_2). For purposes of illustration, the kinetic diameters of the aforementioned gases as well as of two HFC's and a PFC of particular interest - SF6 - are reported hereinafter from Zolands, R. R. and G.K. Fleming, p. 28 in Membrane Handbook, Ho and Sirkar, eds., Van Nostrand Reihnold, 1992.

Table 3: Kinetic diameters of molecules after Breck, in Angstrom

CO_2	O_2	Ar	N_2	SF_6	CF_2Cl_2	CF_4
3.3	3.46	3.4	3.64	5.0 - 5.5	4.3	4.5

Preferred inorganic, molecular sieve membranes are carbon membranes. A suitable carbon molecular sieve membrane can be prepared for example by a method described in PCT application WO 96/22260. Examples of such membranes, having the desired retentivity and permeance parameters, are e.g. those prepared according to steps 1-14 in Table V of Example 1 of said PCT application and those prepared according to steps 1-2 in Table VI of Example 2 of said PCT application, but with a time of 20-75 minutes in step 1.

If necessary, the retentate can be further purified by feeding it to a condenser as taught in EPA 0 754 487. Since higher volume concentration ratios can be obtained by the use of molecular sieve membrane than in other ways, higher temperatures can be used in the condenser, or the feed stream can be less compressed. Since the presence of PFC's and HFC's in the permeate will be extremely low, the permeate can either be directly discharged to the atmosphere or purified by passing it through an adsorber bed, such as sold by suppliers such as Air Products, or through scrubbers such as those supplied by Ecosys. Because of the lower PFC content in the permeate, these permeate purifying devices, if required, can be smaller, or have a longer cycle time between regeneration steps, than similar devices when used in prior art processes. Alternatively, the permeate can be purified, and the residual PFC or HFC contained therein be recovered, by passing said permeate through a second type of membrane, that is permselective to the PFC or HFC over the non-condensable gas, as is taught in PCT WO 92/19359. The resulting concentrated permeate can then be mixed with the feed to the molecular sieve membrane.

The pressure difference on the molecular sieve membrane module can be produced either by compressing the feed gas stream or/and by applying a vacuum on the permeate gas stream.

The retentate can be recycled or otherwise reused as such, or further treated to further increase the content of the PFC or HFC's. The permeate can be discharged to the atmosphere or further purified to recover more PFC or HFC's and make the final waste still more environment-friendly.

The retentate, which has a high concentration of the PFC or HFC's , is available on the feed side of the membrane module, at the high pressure at which it has been fed to said module. It is preferable to maintain said high pressure, either for recycling the retentate to the process which has produced the outlet gas mixture, thus saving compression capital costs and energy needed to store the gas in cylinders, or for sending said retentate to subsequent condensation-purification stages.

The invention further provides an apparatus for the separation and recovery or concentration of perfluorinated compounds, which comprises at least one membrane module installed on the outlet of the duct system of an apparatus in which an industrial process is carried out, and means for recovering the retentate of said module, wherein the permeable membrane of the module has the following characteristics: a retentivity ratio of the PFC or HFC's over nitrogen that is at least 50, and preferably 300, and a permeance for nitrogen that is at least 80 SL/m^2-hr-bar (standard liters per square meter per hour per bar), and preferably at least 200 SL/m^2-hr-bar, provided that if the apparatus is intended for the separation of PFC or HFC's which have a molecular diameter equal to or smaller than that of CHF_3 , the membrane should have a permeance for N_2 which is at least 50 SL/m^2-hr-bar.

The driving pressure for forcing the permeating outlet gases through the membrane can be supplied by the blower gathering the duct gas, by an auxiliary compressor taking the gas from the duct, or by any device for creating a vacuum on the permeate side of the membrane, such as a pump or an ejector. The apparatus further comprises means for returning the retentate gas, leaving the membrane enriched in PFC or HFC, to the process or to further purification apparatus, such as compressor and condenser apparatus.

In an embodiment of the invention, the apparatus further comprises a second membrane module or modules that are permselective for the PFC or HFC's. The term "permselective" is used in the conventional sense used by membranologists, viz. to mean that the gas in question permeates the membrane in preference to other gases in the mixture.

Brief Description of the Drawings

In the drawings:

Fig. 1 shows a typical flow sheet or schematic apparatus illustration using a molecular sieve membrane to recover the PFC or HFC from the effluent, according to an embodiment of the invention;

Fig. 2 shows an embodiment of a two stage membrane process using one compressor and one vacuum pump to provide the transmembrane pressure driving force;

Fig. 3 is a process flowsheet for fabricating a carbon molecular sieve membrane by a combination of pyrolysis followed by one or more CVD and activation steps;

Figs. 4 and 5 are schematic illustrations of apparatus for the recovery of PFC and HFC's from waste gas mixtures, according to two further embodiments of the invention;

Fig. 6 illustrates a typical test system for measuring separating power of the molecular sieve membrane base;

Fig. 7 is a SF_6 vapor pressure diagram;

Fig. 8 is a diagram illustrating SF_6 losses in cryogenic recovery from waste gases; and

Fig. 9 shows diagrams illustrating the effect of membrane selectivity on SF_6 losses.

Detailed Description of Preferred Embodiments

In Fig. 1, block 10 indicates the apparatus of a manufacturing process that produces a PFC or HFC containing effluent. The gaseous feed to the process is indicated as stream 11. It is mixed with recycled gas (stream 12) originating from the recovery apparatus to form the gas feed 13 to the process 10, unless said stream 12 is utilized in any other desired way. The waste gas from the process 14 is collected in a duct system 15. The driving force for collecting the waste gas is provided by the underpressure generated by the inlet to a blower or compressor 16. The waste gas may be diluted by the surrounding air 17 which is also swept into the duct system. At the outlet 18 of the blower or compressor 16, the effluent 18 flows optionally through a guard bed 19 that removes potentially fouling contaminants of the molecular sieve membrane, e.g. moisture. The gas stream then flows into one or more highly productive molecular sieve membrane modules 20, which are highly retentive for the PFC or HFC's. If necessary a vacuum pump 22 can be placed on the permeate (low pressure side or the module) to increase the permeate to feed pressure ratio. The membrane module 20 can actually represent a module array with successively staged concentration steps with gas recycle within each concentration step to provide good flow through the modules. Alternatively the module can represent an array with a tapered flow structure in which there are successively fewer modules in parallel in each successive concentration stage. All of these arrangements are well known to the practitioner of membrane based separations seeking high volume concentration ratios.

In an alternative embodiment, the retentate stream 23 can be sent optionally to a further concentration or purification process such as condensation and/or distillation and/or selective adsorption before being returned to the process. This optional further step is represented by block 26. The permeate 21 can be vented or sent to a further cleaning step such as a scrubber or adsorber (block 30) to remove any vestiges of the PFC or HFC gas.

Fig. 2 represents another preferred embodiment. An effluent stream 31 is fed to a compressor A and the pressurized feed 32 is sent to a first stage membrane module array B operated with the permeate 35 at ambient pressure. Then the concentrated retentate 33 from the first stage is fed to a final membrane concentration stage equipped with molecular sieve membranes C, in which the permeate is maintained at a vacuum to increase the fraction of the more non-condensable gas which is passed to the permeate without a corresponding loss of the PFC or HFC to the permeate. The retentate 34 is used as desired, either by recycling it or in any other way, while the permeate 36 may be sent, if desired, to a further cleaning apparatus D and then vented, as indicated at 37.

A molecular sieve membrane can be prepared with appropriate pore diameter using the techniques reported in the literature for inorganic membranes for gas separation, such as zeolite, amorphous carbon or silicalite materials. For example, a carbon molecular sieve membrane that can be used according to the invention can be prepared by the methods describe in said WO 96/22260 and if necessary with the additional steps described in EPA 94200680.0. The method of preparation is illustrated in the flowsheet of Fig. 3. Said membrane is prepared by first pyrolysing a polymer precursor, such as polyimide or cellulose, which is already in the geometry of a membrane form 51 either in vacuum or in an inert gas stream. The permeability of the resultant carbon membrane can be increased by a series of one or more activation steps 52. In a preferred embodiment, the carbon membrane should have a defined asymmetric structure. If it does not, the thermochemical treatments can include transforming the carbon hollow fiber membrane into an asymmetric membrane by chemical vapor deposition on one of the membrane surfaces 53. Further opening of the carbon matrix to increase the permeability to non-condensing smaller gases can be achieved with further activations 54.

Pure gas permeances were measured by the pressure change method, applying a vacuum to the permeate side of the membrane and measuring the rate of pressure change on the feed side of the membrane module and test apparatus, the volumes of which were previously calibrated. The pressure change is proportional to the molar flux across the membrane:

$dn/dt\ (mol/m^2\text{-}min) = V/RT * dP/dt$

where "n" is the number of moles passing through the membrane. The units "mol/m^2-min" can be converted to SL/m^2-hr, taking into account that 1 mol is equivalent to 22.4 SL. The permeance is then obtained by dividing the molar flux by the average pressure (in bar) found on the feed side of the membrane. It should be noted that the volume on the feed side of the measurement apparatus is arranged to be of such a magnitude that the change of pressure during the measurement period is a small fraction of the total applied pressure so that the transmembrane pressure difference is relatively constant, yet the change is large enough to be accurately measured with the pressure sensors used in the measurement.

A typical treatment which was successful in developing such a membrane is defined in the following table:

Table 4. First set of conditions for making carbon molecular sieve membranes for recovering PFC's

Step	Gas	Temp (° C)	Duration (min)
1	O_2	200	20
2	O_2	270	30
3	H_2	620	10

The next table gives typical results of several carbon hollow fiber molecular sieve membrane modules subjected to this treatment. The results are given as pure gas permeances in SL/m^2-hr-bar, and as selectivities (ratio of N_2 permeance to CF_4 permeance) and were measured as described above.

Table 5: Results of pure gas measurements

Membrane Sample Pyrolysis #	at 25°C			at 200°C		
	P^*N_2	P^*CF_4	Selectivity	P^*N_2	P^*CF_4	Selectivity
372-S1	194	0.31	626	64.305	0.3839	168
372-S2	202	0.12	1683	68.373	0.1284	533
372-S3	250.4	0.077	3252			

*** P means "permeance"**

As can be seen in this table, very high selectivities (>100) are obtained and N_2 permeance is better at room temperature than it is at high temperatures. Measurements were made on other membrane samples prepared in a similar manner and tested on CHF_3 and NF_3 which are the smallest of the PFC and HFC's of high practical interest.

For gases having small molecular diameters, such as CHF_3 and NF_3, and in general, for gases having molecular diameters such as that of CHF_3 or smaller, the process of the invention does not require that the permeable membrane have a permeance for N_2 which is at least 80 SL/m^2-hr-bar, but said permeance may be as low as 50 SL/m^2-hr-bar. An example is shown in Table 6.

Table 6: Separation power of CMSM membrane on the smallest PFC's and CHF's

membrane sample	At 25°C		
	PN_2	$PCHF_3$	Selectivity
1-207/6	76	0.2	380

A comparison of the N_2/PFC selectivities of the carbon molecular sieve membrane with those that can be backcalculated from the glassy polymer aromatic polyimide membranes shows the clear advantage derived from using inorganic, molecular sieve membranes instead of glassy polymeric membranes to recover PFC of HFC's.

Another method of preparation of molecular sieve membranes using a CVD step as well is illustrated in the next table:

Table 7: Alternate protocol for preparation of CMSM for PFC recovery

Step	Gas	Temp (° C)	Duration (min)
1	O_2	200	20
2	O_2	270	30
3	H_2	620	10
4	neopentane	700	5
5	O_2	270	30
6	H_2	620	10

Steps 5- 6 are repeated two more times.

A carbon membrane module prepared with this protocol gave CF_4 permeance at 25 °C of 0.39 SL/m^2-Hr-bar and an N_2 permeance of 310 SL/m^2-Hr-Bar, which gives a selectivity of 795.

Other embodiments of apparatus according to the invention are illustrated in Figs. 4 and 5.

Fig. 4 schematically illustrates an embodiment, in which 10 indicates the apparatus which produces the effluent stream, 13 is the feed to said apparatus, 14 the effluent stream or waste gas produced by apparatus 10, , which may be diluted by surrounding air 17 and is collected in duct system 15, 16 is a blower or vacuum ejector pump providing the driving force for collecting said gas, 18 is the stream outlet by it, 20 is a membrane module or modules for retaining the PCF or HCF, and 21 is the permeate from module 20. The PCF or HCF retentate or concentrate 55 is fed to a compressor 56, then to a condenser composed of a heat exchanger 57 and a liquid-vapor phase separator 58, where the PCF or HCF, which is now in concentrated form, can be more easily compressed and condensed, thereby further purifying it from its non-condensable contaminants. The purified retentate can then be recycled to the process or otherwise used, as indicated at 59, while the waste gases are vented to the atmosphere, as indicated at 60.

Fig. 5 schematically illustrates still another embodiment, wherein the parts that are essentially the same as in Fig. 4 are indicated by the same numerals. In it, the retentate or concentrate stream from membrane module 20, which stream is here indicated at 61, is fed to a second membrane module 62, which is different from module 20 and is permselective for the PFC or HFC's to be separated, viz. selectively permeates them over non-condensable gases. In this embodiment, the enriched retentate presents a higher driving force (the driving force for a given gas being the partial pressure difference across the membrane for that gas) to the membrane 62, which is permselective to the PFC or HFC, and produces a permeate 63 of even higher concentration of these latter, which is recycled or otherwise used. The stream 64 from membrane 62, depleted of PFC or HFC , is recycled to the feed 18 of membrane 20. The permeate 63 of membrane 62 can be used as is, or alternatively fed to a compressor-condenser combination, not illustrated, for further purification of the PFC or HFC from non-condensable gases by conventional means.

Fig. 6 shows a flow system with a gas manifold generally indicated at 41 to provide high pressure gas to the feed side of the membrane module and draw away permeate from the low pressure side of the membrane. The module pressure housing 42 containing the membrane is of stainless steel with bore and shell gas inlet/outlets at each end, so that the module can be operated in bore feed or shell feed mode, as needed. The bore side is kept separate from the shell side by an epoxy potting material in the tube ends, which seals the fibers to each other and to the inner surface of the stainless steel tube.

The feed manifold, generally indicated at 41, comprises three conduits (41-1 through 41-3) connected to pressure gauges 47 and mass flow controllers 44. The permeate rate is measured by mass flow meters or bubble flow meters indicated at 45. The oxygen content of the feed, retentate and permeate streams can be monitored with a Model 570 A Servomex™ oxygen analyzer made by Sybron Corp., indicated by numeral 46. Numeral 47 indicates all pressure gages; numeral 48 indicates pressure transducers and numeral 49 differential pressure transducers. As can be understood from the drawing, this arrangement allows for feeding an arbitrary composition of pure, binary or ternary gas mixtures, and feeding it to the bore side or the shell side and operating the membrane module accordingly. The letters A and B denote positions in which absorbent traps for removal of contaminants can be placed. Other graphic symbols are identified, for the sake of clarity, on Fig. 6.

The process advantages to using inorganic, molecular sieve membranes will be illustrated in the examples.

Example 1: Concentration of N_2/PFC mixture

This example uses the apparatus shown in Fig. 6. The gases N_2 and CF_4 were fed in through the gas manifold 41 using mass flow controllers 41-1 and 41-2. The mixture was fed to the bore side of a hollow fiber module containing 0.16 m^2 of carbon molecular sieve membrane as hereinbefore described. The pressure drop across the membrane is monitored and maintained with the differential pressure gauge 49. The permeate is removed from the shell side outlet of the module that is closest to the feed entrance 50. The pressure in the module feed side is maintained using a backpressure regulator 43. The permeate and retentate feed rates are sampled by the mass flow meters 45b and 45a respectively and fed alternatively to a gas chromatograph 46 to analyze the gas composition.

In this experiment, 1 liter of gas mixture was fed to the module and 0.95 liter was taken out as permeate 50 and 0.05 liter of gas mixture was taken out as retentate 51.

The results of this experiment are shown in Table 8.

Table 8

Feed		Permeate (Molfraction)	Retentate (Mol fraction)
N_2	99.000%	99.998%	80.050%
CF_4	1.000%	0.002%	19.950%
Q(SL/min)	1.00	0.95	0.05
Summary			
Volume concentration factor		20	
% of CF_4 lost to permeate		0.2%	
Pressure ratio (Pf/Pp)		3	

Example 2

The following simulation shows the recovery of PFCs from a process using a system such as shown in Figure 2. The simulation was calculated for a carbon molecular sieve membrane with selectivities as indicated in the tables. The calculation was done assuming crossflow flow pattern and calculating driving forces by a log mean average of inlet and exit conditions, where the local composition of gas on the permeate side is given by the Weller-Steiner equation.

The following tables show the results.

Table 9 - Recovery of Carbon Tetrafluoride

Case: PFC = CF_4

alpha (N_2/PCF) = 500

Stream	31	32	33	34	35	36	37
Composition							
X(N_2)	0.99	0.99	0.9	0.1	0.9999	0.9979	0.9979
X(PCF)	0.01	0.01	0.1	0.9	0.0001	0.0021	0.0021
Conditions							
P (bars)	1.05	7	7	7	1	0.1	1
Q (Nm^3/hr)	10	10	0.991	0.108	9.009	0.883	0.883

Summary of the Process

	Stage 1	Stage 2	Total
CF_4 loss	0.88%	1.87%	2.75%
Module area (m^2)	8	2	10
Compressor power KW	1.13	0.125	1.255

Table 10 - Recovery of nitrogen trifluoride

Case: PFC = NF_3

alpha (N_2/PCF) = 75

Stream	31	32	33	34	35	36	37
				Composition			
X(N_2)	0.99	0.99	0.9	0.1	0.9994	0.9861	0.9861
X(PCF)	0.01	0.01	0.1	0.9	0.00065	0.0139	0.0139
				Conditions			
P (bara)	1.05	7	7	7	1	0.1	1
Q (Nm^3/hr)	10	10	0.940	0.091	9.06	0.849	0.849

Summary of the Process

	Stage 1	Stage 2	Total
PFC loss	5.87%	11.78%	17.66%
Module area (m^2)	8	2	10
Compressor powerKW	1.13	0.125	1.255

Among the PFC's to which the invention refers, SF_6 is of particular interest. When recovering SF_6, it is preferable to retain it and pass the permanent gases through, since the permanent gases are to be vented to the atmosphere in most cases, while the SF_6 is to be recovered and it is desirable to recover it at pressure. Since the most common contaminant to be found with SF_6 is air, which is made up largely of nitrogen, it is convenient to define the selectivity of the membrane as the selectivity between SF_6 and nitrogen. The required selectivity will depend on the concentration of SF_6 and the concentration factor required to return it to the process. The higher the concentration factor, the higher the selectivity required to prevent significant SF_6 losses.

One of the advantages of the molecular sieving membranes from inorganic materials is that their matrices are fixed and defined at a wide range of temperatures and do not undergo swelling when permeated by molecules that interact with the matrix.

The required selectivity is a function of the concentration of the SF_6 in the waste gas and the concentration factor by which it must be raised in the recovered product gas. The higher the ratio of concentrations in product to waste gas the greater the demand of retentive selectivity for SF_6 and the higher the initial SF_6 concentration in the waste gas the greater the losses. For example if a membrane has an SF_6/air retentivity ratio of 50 and the feed-to-permeate pressure ratio is 10, then the following losses of SF_6 result in concentrating the waste gas to recovery the SF_6:

SF_6 conc. in waste gas	SF_6 conc in product gas	Concentration ratio	Loss of SF_6 to permeate
0.8%	8%	10	8.3%
0.08%	8%	100	49.8%
8.0%	80%	10	19.6%

A carbon sieve membrane that can be used according to the invention for separating SF_6 from other, particularly non-condensable gases, can be prepared, as has been said, by the method described in said WO 96/22260, and if necessary with the additional steps described in EPA 94200680.0, e.g. as follows. Said membrane is prepared by a series of thermochemical treatments of a carbon hollow fiber membrane which has previously been formed by pyrolyzing a non-melting polymer such as cellulose in an inert gas stream. In a preferred embodiment, the carbon hollow fiber membrane should have a defined asymmetric structure. If it does not, the thermochemical treatments include firstly transforming the carbon hollow fiber membrane into an asymmetric membrane by chemical vapor deposition on one of the membrane surfaces. This can optionally be preceded by one or more (preferably only one) mild activation steps (exposure to an oxidant at temperatures of 200-250°C for 10-50 minutes). Following the transformation of the membrane into an asymmetric membrane, its permeance is then increased by a series of activations by exposing it to oxygen at temperatures ranging from 200 to 300°C and times ranging from 10 to 90 minutes. .After each activation, residual oxygen is removed by treating the membrane with hydrogen or other reducing gases at elevated temperatures. These activation steps are continued until the required permeance to the slowest non-condensable gas (e.g. N_2) is achieved, as indicated by the point at which the selectivity between oxygen and nitrogen drops to less than 2 and preferably to less than 1.5.

The pure gas permeances were measured by the pressure change method, applying a vacuum to the permeate side of the membrane and measuring the rate of pressure change on the feed side of the membrane module and test apparatus, the volumes of which were previously calibrated. The pressure change is proportional to the molar flux across the membrane:

$$dn/dt\ (\mathrm{mol/m^2 \cdot min}) = V/RT * dP/dt$$

wherein "n" is the number of moles passing through the membrane. The units "$\mathrm{mol/m^2 \cdot min}$" can be converted to $\mathrm{SL/m^2}$-hr, taking into account that 1 mol is equivalent to 22.4 SL. The permeance is then obtained by dividing the molar flux by the average pressure (in bar) found on the feed side of the membrane. It should be noted that the volume on the feed side of the measurement apparatus is arranged to be of such a magnitude that the change of pressure during the measurement period is a small fraction of the total applied pressure so that the transmembrane pressure difference is relatively constant, yet large enough to be accurately measured with the pressure sensors used in the measurement.

A typical treatment which was successful in developing such a membrane is defined in the following table:

Table 11

Preparation protocol for membrane effective in SF_6 recovery

Step	Gas fed	Temp (°C)	Duration
1	O_2	200	20
2	neo-pentane	700	3
3	O_2	280	75
4	H_2	620	10
5	O_2	280	60
6	H_2	620	10
7	O_2	280	45
8	H_2	620	10

The said membrane has the pure gas permeances set forth in Table 12.

Table 12

Permeation characteristics of carbon molecular sieve membrane(CMSM) preferred for SF_6 recovery

Gas	Permeance (SL/m^2 -hr-bar)	Permeance Ratio Fast Gas/ SF_6
Oxygen	1600	16,000
Nitrogen	929	9290
SF_6	0.1	

If desirable, the membrane can be opened in one additional activation step to increase the permeability to the slowest of the non-condensable gases, which is N_2 in this case, but at the expense of selectivity. An additional step will result in the increase of nitrogen permeance to 1300 SL/m^2-hr-bar, but at the cost of the N_2/SF_6 permeance ratio dropping to 810.

The effect of selectivity on loss of SF_6 to the permeate gases 21, as a function of volume concentration factor (CF), which is the ratio of the input feed rate 18 to the output retentate rate 12, is shown in Fig. 9. α is the retentivity of SF_6 over nitrogen.

A module composed of a pressure vessel of the length of about 2.7 m and diameter of 0.2 m, in which were potted 70,000 hollow fibers of carbon molecular sieve membrane with about 85 m^2 area with an average fast gas permeance of 1300 SL/m^2-hr-bar, could process 200 Nm^3/hr of a stream at 3 bara containing 2% SF_6 by concentrating it tenfold. Higher concentration factors would require higher feed pressures, or larger areas. By comparison, if it were wished to treat under the same operating conditions the aforesaid feed stream, so as to retain SF_6 by means of modules suitable for air separation (O_2/N_2 selectivities of 5-7 and permeances of 100-150 SL/m^2-hr-bar), 10 modules of the same dimension would be required, which would be prohibitive. This indicates the importance of choosing the correct membrane type and membrane preparation.

The O_2 partial pressure driving force is calculated from the measured transmembrane pressure and the measured O_2 content in feed, retentate and permeate streams. Where binary SF_6/O_2 mixtures are separated, the SF_6 content of each stream is calculated by the difference, $1-X_{O2}$. The expression $1-X_{O2}$ means the mol fraction of the gas mixture which remains after subtracting the mol fraction of oxygen. Thus, for a binary mixture of SF_6 and O_2, the mol fraction of SF_6 is given by $1-X_{O2}$.

A carbon molecular sieve membrane was subjected to thermochemical treatments according to the general procedure described in said WO 96/22260. The membrane thus prepared, composed of a bundle of 100 fibers having an area of 0.18 ft^2, was loaded in a high pressure housing formed of a ¼ inch stainless steel tubing with end tube fittings to allow separate access to the bore and shell side of the membrane bundle. This membrane module was then mounted on the mixed gas test system described in Fig. 6.

The following, non-limitative Examples illustrate embodiments of the invention carried out by means of said gas test system.

Example 3

A carbon molecular sieve membrane with appropriate selectivity for SF_6 recovery was prepared according to the preparation conditions summarized in the following Table 13.

Table 13

Step	Gas fed	Temp (°C)	Duration (min)
1	O_2	200	20
2	neo-pentane	695	5
3	O_2	270	30
4	H_2	620	10
5	O_2	280	50
6	H_2	620	10
7	O_2	280	40
8	H_2	620	10
9	O_2	280	40
10	H_2	620	10
11	O_2	280	40
12	H_2	620	10
13	O_2	280	60
14	H_2	620	10

It was then potted in a pressure housing and the resultant module was mounted on the test system hereinbefore described. Sequentially, ~1 SL/min first of oxygen and then of SF_6, were fed under a transmembrane pressure difference of 1.28 bar to the bore side of the module and the flow rate of the permeate issuing from the shell side was measured. The pressure was maintained using a back pressure regulator on the retentate flow stream.

The results of this test are in the following Table 14.

Table 14

Gas	Permeate flow rate (scc/min)	Permeance (SL/m^2-hr-bar)
O_2	700	1600
SF_6	Not detectable	Not detectable

Subsequent measurement of the membrane module with pure oxygen again showed that the pure oxygen permeance had not fallen, but had even slightly risen. This shows that the SF_6 which may have adsorbed on the membrane did not interfere with oxygen permeance.

Example 4

A carbon molecular sieve membrane with appropriate selectivity for SF_6 recovery was prepared according to detailed preparation conditions, as summarized in the following Table 15.

Table 15

Preparation of membrane batch 454/2

Step	Gas fed	Temp (°C)	Duration
1		25	
2	neo-pentane	700	3
3	O_2	280	75
4	H_2	620	10
5	O_2	280	60
6	H_2	620	10
7	O_2	280	45
8	H_2	620	10
9	O_2	280	30
10	H_2	620	10

This membrane was mounted in a stainless steel pressure housing and mounted on the gas test system hereinbefore described. The pure oxygen permeance was measured and found to be 1118 SL/m^2-hr-bar. When the same membrane was fed SF_6 to the bore, no permeation could be detected, as seen by the absence of bubbles in a bubbler attached to the permeate port of the module.

Subsequently, the module was fed a mixture (v/v%) of 98% O_2 and 2% SF_6 to the bore side at a pressure of approximately 3 bar transmembrane pressure. Because the oxygen monitor was not sensitive enough to reliably measure with +/- 0.1% at values above 98%, the O_2 content of the permeate was calculated from the O_2 mass balance, and the SF_6 content was calculated by the difference. The results are summarized in the following Table 16.

Table 16

Results of mixed gas experiment on CMSM module

Raw Data	Feed	Permeat*	Retentate
Q(scc/min)	437.4	428	9.42
XO_2 (mol %)	98%	99.77%	18%
XSF_6 (mol %)	2%	0.23%	83%
*O_2 composition of permeate calculated from O_2 mass balance			
Calculated Results			
SF_6 Conc Ratio		45.833	
VCF (Qf/Qp)		46.435	
%SF_6 Recovered		89%	
O_2 Permeance		1214.7	

This shows the power of the membrane to highly concentrate the SF_6 while losing only a small portion of it to the permeate.

Example 5 - Recovery of SF_6 from a light metals foundry

Reference is made to Fig. 1. In a foundry where light metals are cast, SF_6 is used to protect the surface of the cast metal. For a particular plant, the SF_6 content of the protective gas mixture (stream 13) fed at 10 m^3/hr to the casting cell is 1% (v/v) and the exit gas (stream 14) is diluted by the blowers collecting the exit gas to 0.05% (v/v) with a flow of 200 m^3/hr. The SF_6 gas is recovered by compressing the waste gas stream to 3 bara (stream 18) and passing the fast gases through the membrane module (stream 21) and returning ~10 m^3/hr of SF_6 enriched retentate (stream 23) back to the casting cells as stream 12 where makeup SF_6 can be added (as stream 11). The membrane has the permeation characteristics listed in Table 12. The flow and composition balance of the stream of this example are given in the following Table 17.

Table 17

Stream flows and SF_6 content in recovery from foundry blanket gases

Stream #	11	12	13	14	18	21	23
Flow rate Nm^3/Hr	0.5	9.5	10	10	200	190	9.5
ppm (v/v) SF_6	1.00E+04	9999.6	1.00E+04	9500	500	0.4	9999.6
Pressure, bara	1.33	1.33	1.33	1	3.2	1	3.2

As can be seen by comparing the SF_6 content in stream 18 with that of stream 21, by using such a membrane in such an application, the waste SF_6 released to the atmosphere is reduced by three orders of magnitude.

Example 6 (comparative)

This example shows the impracticality of recovering SF_6 by purely cryogenic means. If there is a process effluent stream that contains 5% SF_6 mixed with a non-condensable gas or gases and at least 80% of the SF_6 in this stream should be recovered, then the following Table 18, generated by using the data found in the vapor pressure curve (Fig. 7), lists different minimal conditions that would be needed to recover at least 80% of this stream. This table can be read as the maximal temperatures allowed for a particular pressure to which the effluent stream has been compressed, or as the minimum pressure to which the effluent stream has been compressed, or as the minimum pressure to which the effluent stream must be compressed if the minimum temperature in the condenser is as listed in the following table.

Table 18

Conditions for cryogenic recovery of 80% of SF_6 from stream containing 5% SF_6

T (°C)	P(Bara)
-102	5
-94	10
-77	40

If this same effluent gas were to be pre-concentrated with the membrane module in Example 5 to 50% SF_6 and then further compressed and condensed, milder conditions could be used to attain the same 80% SF_6 recovery. This can be illustrated with reference to Fig. 4. The following stream table with conditions and concentrations illustrates the point. The stream numbers refer to those in Fig. 4. Stream number 31 has been added to refer to the retentate stream after it has been compressed in an isothermal compressor to 5 bara before being sent to the condenser.

Table 19

Flows and SF_6 content of streams in combined membrane and cryogenic recovery of SF_6

Stream #	18	21	55	31	59	60
Flow rate, mol/hr	4500	4050	450	450	180	270
mol% SF_6	5.0%	0.3%	50.0%	50.0%	100.0	16.7%
SF_6 flow rate, mol/hr	225	11	225	225	180	34
Pressure (bara)	2	1	2	5	5	5
Temp °C	25	25	25	25	-76.8	-76.8

As can be seen in comparison to Table 18, the concentrated waste stream need only be condensed to 5 bar instead of 40 bar for a final condensation temperature of -77, and only 450 mol/hr instead of 4500 mol/hr need be compressed, a tremendous savings in compression energy. Also, the compression ratio is half what it would be if ambient pressure gas were compressed, since the retentate is already at 2 bara.

Example 7

A membrane is prepared in a similar manner as in example 4. This membrane was then mounted in a stainless steel housing and tested in a gas mixture test system, hereinbefore described and illustrated in Example 3. However, in the present example the feed gas contained 91% O_2 and 9% CHF_3. The feed was fed to the shell side of the membrane at 7 bar absolute pressure and the bore side was maintained at 1 bar absolute pressure, giving a pressure ratio of 7. Measurements and calculations where made in a manner similar to example 4. The results are given in Table 20.

Table 20: Results of test separating mixture of CHF_3 and O_2

T (°C)	120
P in	7
P out	1
Pressure Ratio	7

STREAM	XO_2	$XCHF_3$	Q (scc/min)
Feed	91.8%	8.2%	172
Permeate	100.0%	ND	136
Retentate	61.0%	39.0%	36
Volume conc. ratio			4.8
% CHF_3 lost to permeate			0.45%

X_i represents mole %

It can be seen comparing this result to example 1 of EPA 0 754 487 that CHF_3 is retained to a much greater degree.

CLAIMS

1 - Process for the separation and recovery or concentration of PFC's and HFC's from gaseous streams of manufacturing processes which contain PFC or HFC, which comprises the steps of:

a) bringing the gaseous stream into contact with a membrane module at a first pressure, high pressure;

b) drawing the permeate in such a way as to maintain a second pressure, lower than said first pressure, on the permeate side of the module; and

c) recovering the retentate;

d) characterized in that the membrane is an inorganic molecular sieve membrane, which passes nitrogen but not PFC and HFC molecules, and has a retentivity ratio of the PFC or HFC molecule over nitrogen that is at least 50, and preferably 300, and a permeance for nitrogen that is at least 80 SL/m^2-hr-bar (standard liters per square meter per hour per bar),. and preferably at least 200 SL/m^2-hr-bar, provided that if the PFC or HFC has a molecular diameter equal to or smaller than that of CHF_3 , the permeance of the membrane for N_2 is at least 50 SL/m^2-hr-bar.

2. Process according to claim 1, wherein the molecular sieve membrane is chosen from among inorganic, microporous, molecular sieve having a pore size larger than the effective molecular diameter of the non-condensable gases present in the gaseous stream.

3. Process according to claim 2, wherein the molecular sieve membrane has a pore size of at least 3.7 *Angstrom*.

4. Process according to claim 1, wherein the inorganic molecular sieve membrane is a carbon membrane.

5. Process according to claim 1, preparing the carbon molecular sieve membrane by a method described in PCT application WO 96/22260.

6. Process according to claim 1, further comprising purifying the retentate.

7. Process according to claim 1, further comprising purifying the permeate.

8. Process according to claim 6, further comprising purifying the retentate by feeding it to a condenser.

9. Process according to claim 1, comprising discharging the permeate directly to the atmosphere.

10. Process according to claim 7, wherein the permeate is purified by passing it through an adsorber bed

11. Process according to claim 1, further comprising recycling the retentate.

12. Process according to claim 6, comprising further purifying the retentate by combined compression and condensation.

13. Process according to claim 1, comprising recovering residual PFC or HFC from the permeate of the molecular sieve membrane by passing it through a second membrane, that is permselective to the PFC or HFC over the non-condensable gas, and mixing the permeate from said second membrane, enriched with PFC or HFC, with the feed to said molecular sieve membrane.

14. Process according to claim 1, wherein the pressure difference on the molecular sieve membrane module is produced either by compressing the feed gas stream or/and by applying a vacuum on the permeate gas stream.

15. Process according to claim 1, wherein the PFC is chosen from among SF_6, NF_3, WF_6, CF_4, and C_2F_6.

16. Process according to claim 1, wherein the HFC is CHF_3.

17. Process according to claim 15, wherein the PFC is SF_6

18. Process according to claim 1, further comprising feeding the retentate to at least a second membrane module with permselectivity for the PFC or HFC.

19. Process according to claim 17, wherein the recovered retentate, optionally after further purification, is used in a semiconductor manufacturing process.

20. Process according to claim 17, wherein the recovered retentate, optionally after further purification, is used for reactive ion etching or post-etching treatment in particular.

21. Process according to claim 17, wherein the recovered retentate, optionally after further purification, is used in Mg and aluminum foundries or manufacturing plants.

22. Process according to claim 17, wherein the recovered retentate, optionally after further purification, is used as an insulating gas in electric power and transmission industries.

23. Process according to claim 2, wherein the membrane has such a maximum pore size as to retain the PFC or HFC that it is intended to recover.

24. Process according to claim 23, wherein the maximum pore size is 5.5 Angstrom.

25. Process according to claim 2, wherein the permeable membrane is chosen from among inorganic, microporous, molecular sieve membranes having a pore size of 3.7 to 5.5 Angstrom.

26. Apparatus for the separation and recovery or concentration of PFC and HFC's from gas mixtures, in particular waste gas streams issuing from the duct system outlet of an apparatus in which an industrial process is carried out, which comprises at least one membrane module installed on said outlet and means for recovering the retentate of said module, wherein the permeable membrane of the module the membrane is an inorganic, molecular sieve membrane, which has a retentivity ratio of the PFC or HFC molecule over nitrogen that is at least 50, and preferably at least 300, and a permeance for nitrogen that is at least 80 SL/m^2-hr-bar (standard liters per square meter per hour per bar), and preferably at least 200 SL/m^2-hr-bar, provided that if the apparatus is intended for the separation of PFC or HFC's which have molecular diameters equal to or smaller than that of CHF_3 , the membrane has a permeance for N_2 which is at least 50 SL/m^2-hr-bar.

27. Apparatus according to claim 26, wherein the molecular sieve membrane is chosen from among inorganic, microporous, molecular sieve membranes having a pore size larger than the effective molecular diameter of the non-condensable gases present in the gas stream.

28. Apparatus according to claim 26, wherein the sieve membrane has a minimum pore size of at least 3.7 *Angstrom*.

29. Process according to claim 26, wherein the molecular sieve membrane is a carbon membrane.

30. Apparatus according to claim 26, wherein the membrane has such a maximum pore size as to retain the PFC or HFC that it is intended to recover.

31. Apparatus according to claim 26, further comprising at least a second membrane module with permselectivity for the PFC or HFC's.

32. Use of a permeable membrane, chosen from among inorganic, microporous, molecular sieve membrane having retentivity ratio of the PFC or HFC molecule over nitrogen that is at least 50, and preferably at least 300, and a permeance for nitrogen that is at least 80 SL/m^2-hr-bar (standard liters per square meter per hour per bar), and preferably at least 200 SL/m^2-hr-bar for the separation and recovery of PFC and HFC's from gas mixtures, in particular waste gas streams from industrial processes.

33. Use of a permeable membrane, chosen from among inorganic, microporous, molecular sieve membrane having retentivity ratio of the PFC or HFC's molecules over nitrogen that is at least 50, and preferably at least 300, and a permeance for nitrogen that is at least 50 SL/m^2-hr-bar (standard liters per square meter per hour per bar, for the separation and recovery or concentration of PFC and HFC's having a molecular diameter equal to or smaller than that of CHF_2 , from gas mixtures, in particular waste gas streams from industrial processes.

34. Use of a permeable membrane accordin g to claim 32, wherein the permeable membrane has a minimum pore size of 3.7 Angstrom.

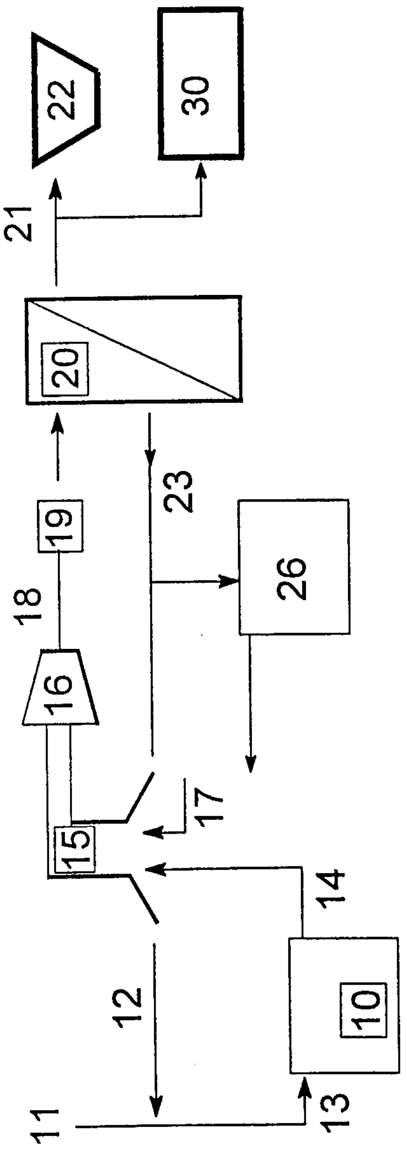

Fig. 1

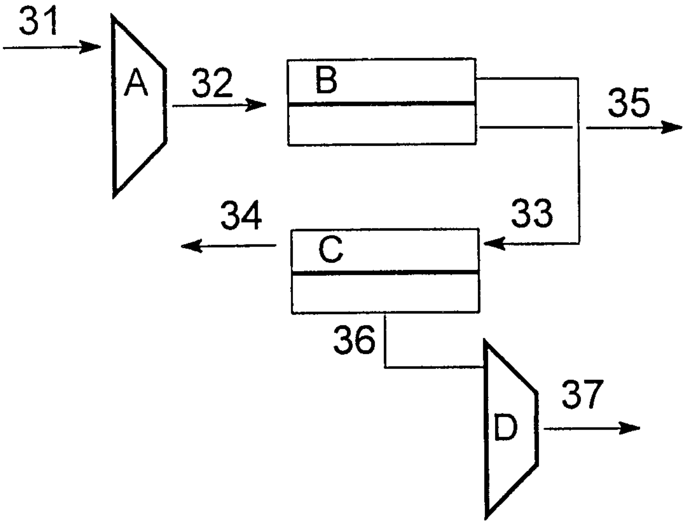

Fig. 2

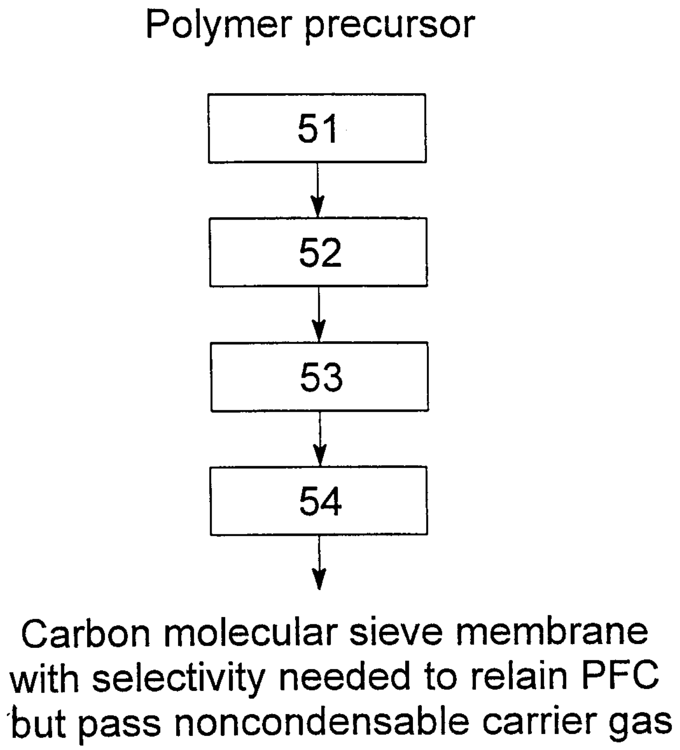
Polymer precursor
51
52
53
54
Carbon molecular sieve membrane with selectivity needed to relain PFC but pass noncondensable carrier gas

Fig. 3

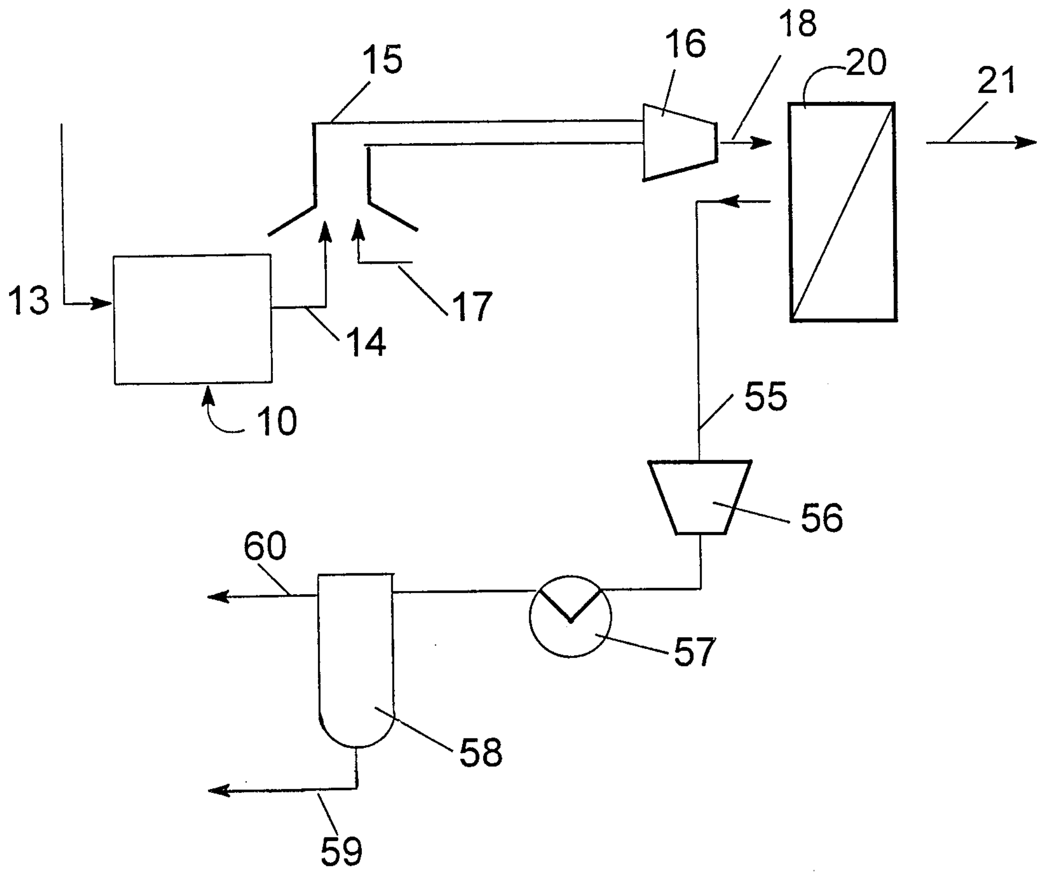

Fig. 4

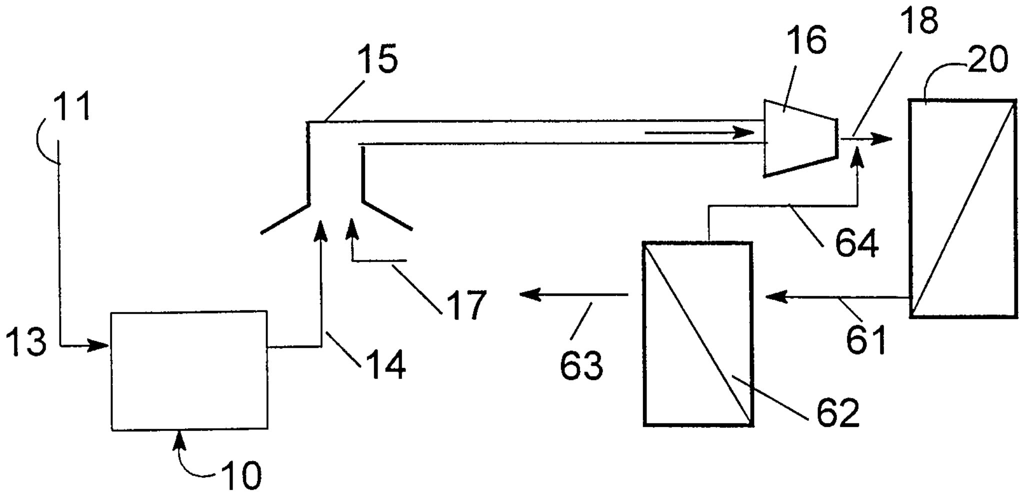

Fig. 5

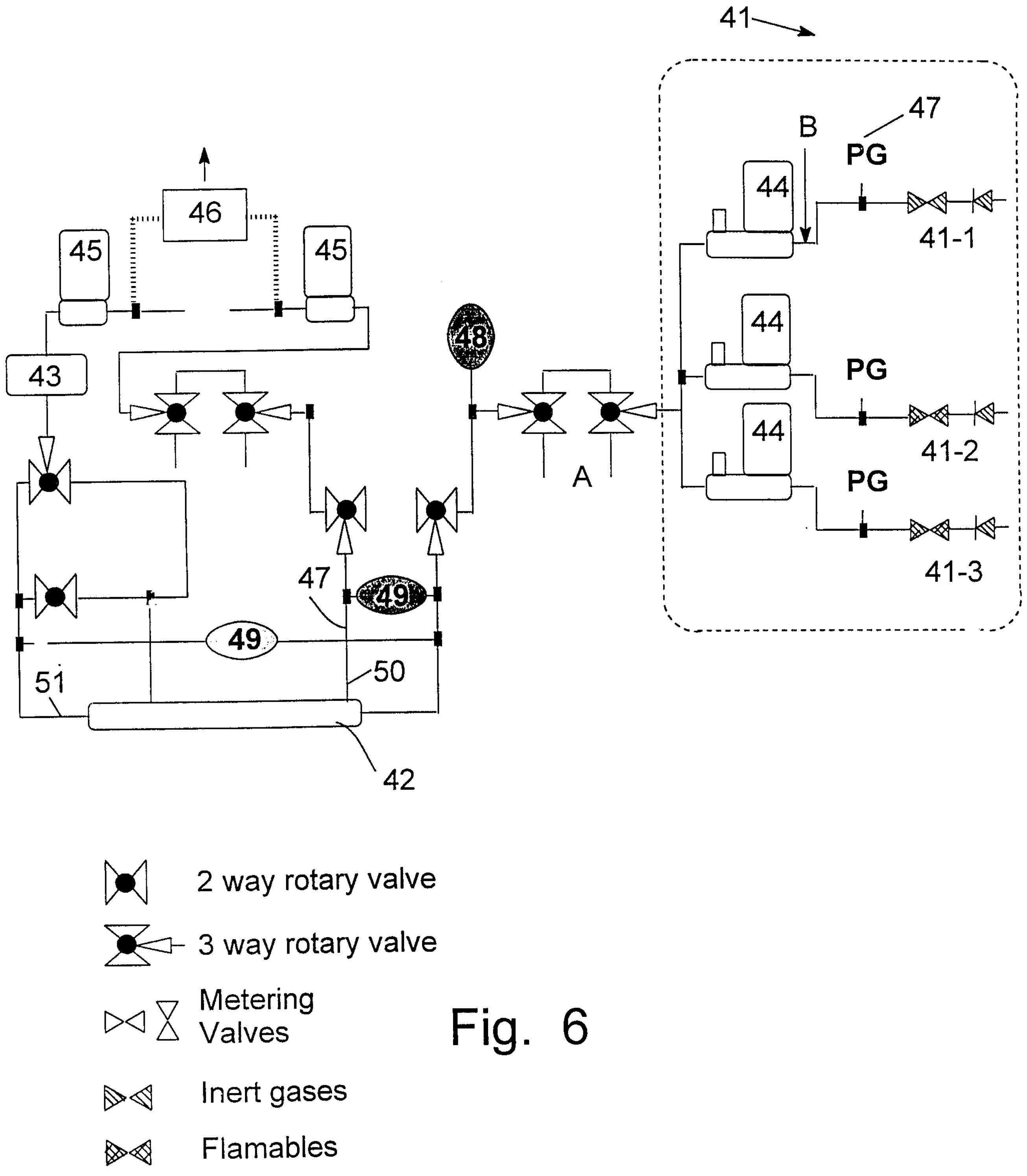
41
47
B
PG
44
41-1
46
45
45
48
44
PG
43
44
41-2
A
PG
41-3
47
49
49
50
51
42
2 way rotary valve
3 way rotary valve
Metering Valves
Inert gases
Flamables

Fig. 6

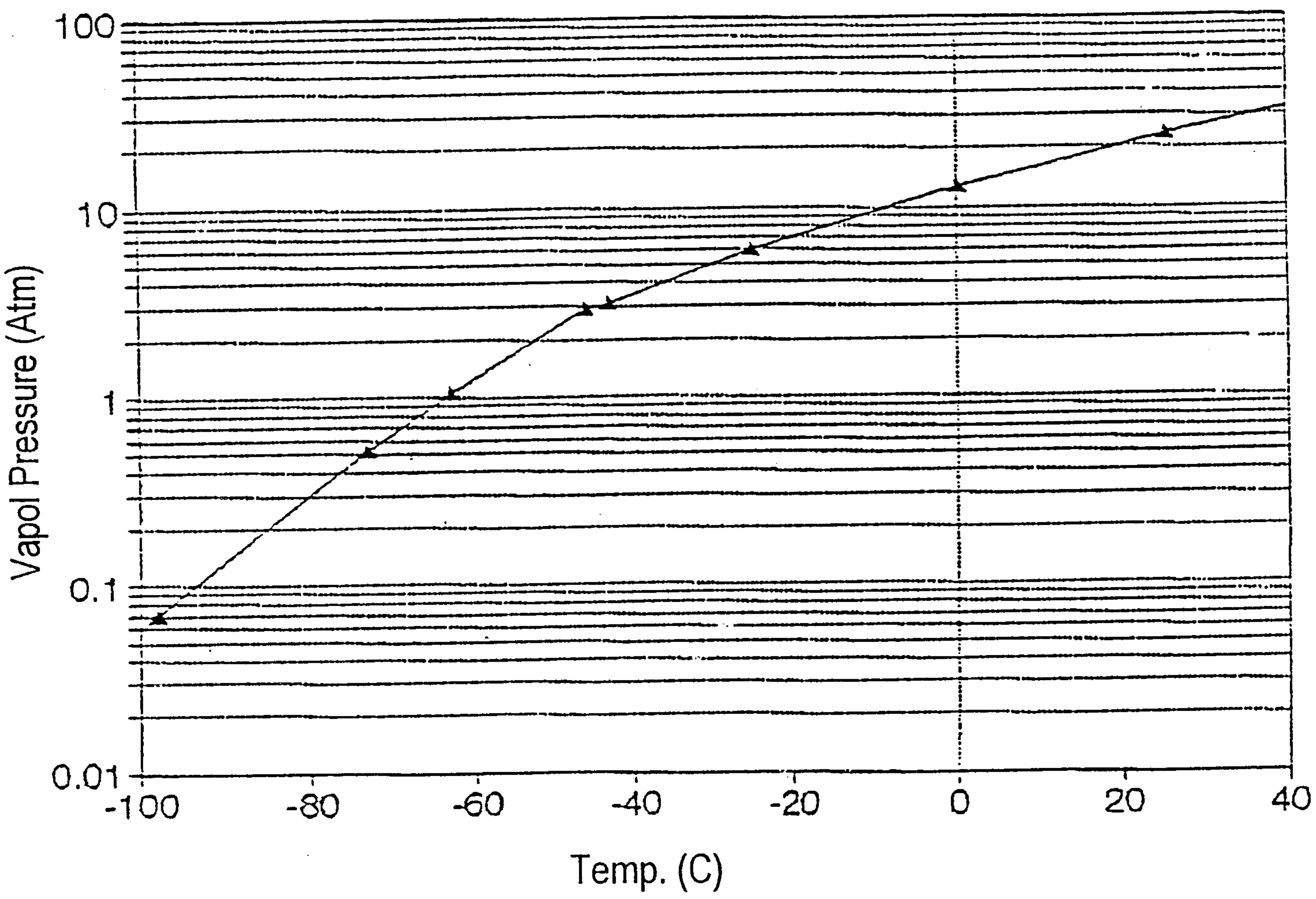

Fig. 7

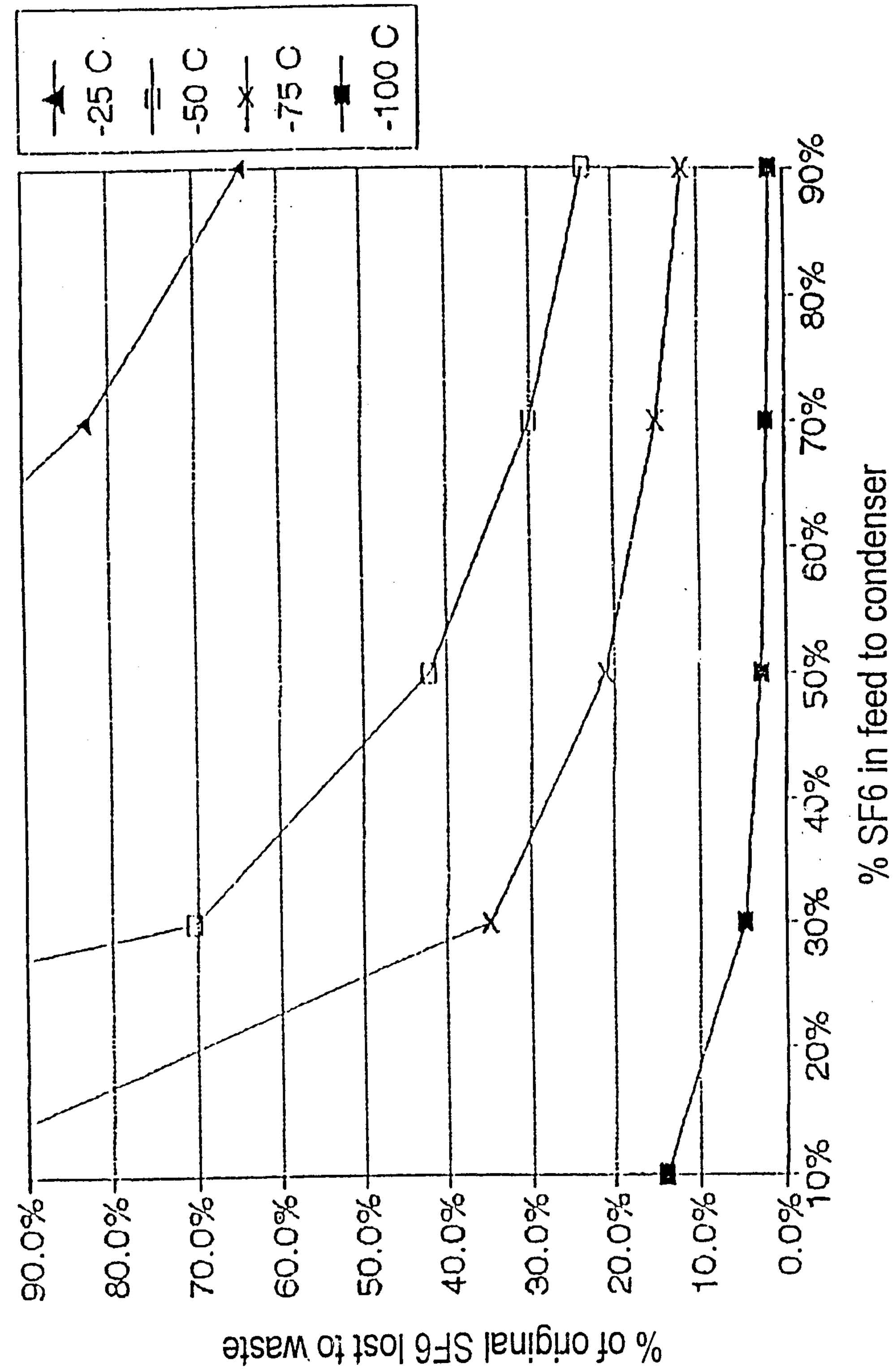
-25 C
-50 C
-75 C
-100 C
90.0%
80.0%
70.0%
60.0%
50.0%
40.0%
30.0%
20.0%
10.0%
0.0%
% of original SF6 lost to waste
10%
20%
30%
40%
50%
60%
70%
80%
90%
% SF6 in feed to condenser

Fig. 8

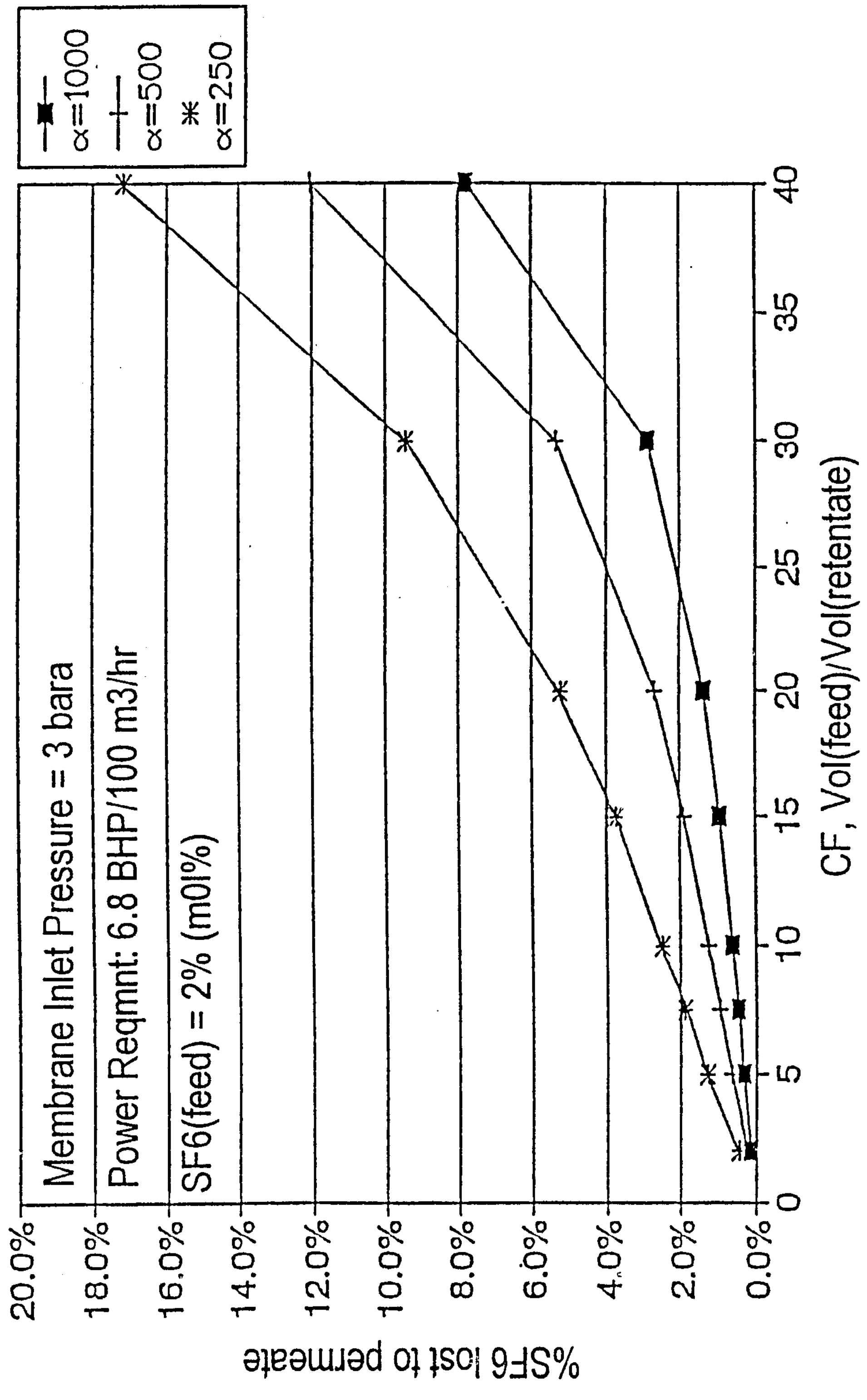
α=1000
α=500
α=250
Membrane Inlet Pressure = 3 bara
Power Reqmnt: 6.8 BHP/100 m3/hr
SF6(feed) = 2% (m0l%)
%SF6 lost to permeate
20.0%
18.0%
16.0%
14.0%
12.0%
10.0%
8.0%
6.0%
4.0%
2.0%
0.0%
0
5
10
15
20
25
30
35
40
CF, Vol(feed)/Vol(retentate)

Fig. 9

INTERNATIONAL SEARCH REPORT

International application No.
PCT/IL98/00030

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :B01D 53/22
US CL :95/47, 50; 96/4,9
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)

U.S. : 95/39, 45, 47-55; 96/4,7,9

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

NONE

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

NONE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5,226,932 A (PRASAD) 13 July 1993 (13.07.93) Figures 1-2.	1-34
A	US 5, 282,969 A (XU) 01 February 1994 (01.02.94) Figures 2-3.	1-34
A	US 5,354,547 A (RAO ET AL) 11 October 1994 (11.10.94) Figures 2-4.	1-34
A	US 5,482,539 A (CALLAHAN) 09 January 1996 (09.01.96) Figures 2-3.	1-34
A,P	US 5,649,996 A (SOFFER ET AL) 22 July 1997 (22.07.97) Figure 2A.	1-34
A,E	US 5,730,779 A (CHERNYAKOV ET AL) 24 March 1998 (24.03.98)	1-34

☐ 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 published on or after the international filing date
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"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

07 MAY 1998

Date of mailing of the international search report

18 JUN 1998

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