II. INTRODUCTION OF ECOLOGICAL CONSIDERATIONS INTO CHEMICAL AND OTHER INDUSTRIES

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Certain possibilities of gas-separating membranes for the creation of ecologically clean industries

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The problems of the separation or purification of natural, technological, and exhaust gases have now become especially acute (particularly due to the imperfection of the existing technologies). Certain problems of industrial technology can be solved with the aid of the membrane separation of gases, which constitutes in essence an ecologically clean method.

The assortment of industrial gas-separating membranes, elements, and devices available throughout the world is not as yet very great but, bearing in mind certain advantages of membrane processes, many firms (chemical companies, manufacturers of membranes, suppliers of gases, and engineering firms) have expanded wide-scale research into the membrane separation of gases. According to the prediction by the Day Chemical Company, the scale of the manufacture of gas-separating modules has increased from ten million dollars in 1985 to 145 million dollars in 1990. The separation of gases with the aid of membranes is based on the different rates of transport of gaseous components through polymer membranes due to the [different?] gradients of their partial pressures (concentrations).

A characteristic feature of membrane gas separation processes is the flow regime of their operation. A readily permeable component, for example, a harmful component, can be "removed" from the stream of gaseous raw material entering the membrane module, obtaining at one outlet from the membrane module an ecologically cleaner mixture and at the other outlet (beyond the membrane) a stream enriched in the harmful component to be utilised further or used in recycling. The degrees of extraction and sampling of the components can be varied within wide limits, but, when account is taken of the driving force of the process (partial pressure), it is most convenient to use membranes for the depletion or enrichment of gaseous mixtures with a high content of the components to be separated. At the same time, thorough single-stage purification of gas mixtures by membrane methods cannot as yet compete with alternative methods, for example, the reagent procedures.

It appears that the membrane separation of gases can be used in the solution of ecological problems in the following versions: the isolation and removal of harmful components from gaseous waste; the incorporation of membrane processes in the technology for the prevention of the formation of side products; the application of autonomous membrane devices in processes for the intensification of purification stages.

Table 1. The permeability and selectivity of certain industrial gas-separating membranes.

Type of membrane	Q, litres $m^2\ h^{-1}\ atm^{-1}$					
	H_2	O_2	N_2	CH_4	CO_2	CO
Asymmetric planar polyvinyltrimethylsilane membrane (Institute of Petrochemical Synthesis of the USSR Academy of Sciences, "Plastmassy" Scientific-Industrial Association, 1975)	2500	580	160	260	2000	160
Composite polysulphone hollow fibre (Monsanto Corporation, USA, 1979)	151	22.7	3.8	6.3	104	6.6
Composite planar membrane based on a ternary copolymer comprising fluorinated polymers (Asahi Glass Company, Japan, 1982)	1900	560	140	220	2300	–
Composite planar membrane based on cross-linked polysiloxanes (Asahi Glass Company, Japan, 1980)	4100	3400	1800	5200	13000	–

In the construction of devices, these versions are achieved by inserting membrane devices (modules) in the gaseous "tails" of exhausts from technological processes, or by incorporating membrane modules in the technological scheme for the process, or by using gas mixtures prepared autonomously by membrane methods with intensification of the stages involving the purification of solid and liquid waste. The main gas separating polymer membranes used in industry are described above (Table 1).

The asymmetric planar polyvinyltrimethylsilane (PVTMS) has been developed at the Topchiev Institute of Petrochemical Synthesis (IPS) of the USSR Academy of Sciences and has been manufactured since 1975 by the "Plastmassy" (Plastics) Scientific-Industrial Association. The membrane has been used in processes designed to enrich air in oxygen, in the isolation of hydrogen from its mixtures with nitrogen, methane, and carbon monoxide, and for the separation of mixtures of carbon dioxide and methane. Certain parameters of its permeability are presented in Table 1.

The Monsanto Corporation (USA) manufactures an asymmetric composite polysulphone hollow fibre designed for the industrial separation of water-containing gas mixtures. The membrane modules of this firm are partly used also for the enrichment of oxygen in air.

The anisotropic composite planar membranes of the Asahi Glass Company (Japan) are used mainly for the enrichment of oxygen in air and in processes designed to regulate the composition of a gaseous medium.

New polymer materials for gas-separating membranes are being vigorously investigated in world laboratories. These are, for example, silane-containing block copolymers, polytrimethylsilylpropyne (it has the most effective gas-permeability parameters among the known polymers), and siloxane-containing and other polymeric materials (Table 2). It is noteworthy that the mixtures to be separated consist, with rare exceptions, of permanent gases the diffusion of which in the membrane does not entail specific interactions. On the other hand the separation of, for example, acid gases requires the creation of materials which operate stably under severe chemical conditions. This problem is at present in the development stage (see polyamidoimides in Table 2).

Table 2. Certain experimental specimens of gas-separating membranes tested in world laboratories.

Polymeric materials	Mixtures separated
Silane-containing copolymers (Institute of Petrochemical Synthesis of the USSR Academy of Sciences)	Permanent gases, hydrocarbons
Polytrimethylsilylpropyne (Sanyo Chemical Industry, Japan; Air Products, USA; Institute of Petrochemical Synthesis of the USSR Academy of Sciences)	Air, biogas
Siloxane-containing and other polymers (General Electric Corporation, USA; Polimersintez Scientific-Industrial Association, Mendeleev Moscow Institute of Chemical Engineering, USSR)	Oxygen, nitrogen, carbon dioxide
Poly-4-methylpent-1-ene (Khimvolokno Scientific-Industrial Association, USSR: Torei Company, Japan)	Oxygen, nitrogen, carbon dioxide
Poly(phenylene oxide) (General Electric Corporation, USA)	Air
Polyamidoimides (Ube Company, Japan; Institute of Macromolecular Compounds of the USSR Academy of Sciences)	Hydrogen, acid gases

One of the examples of the membrane separation of gaseous waste is the separation of biogas (Fig. 1). This problem is particularly urgent in large cities where giant plants for the processing of waste are being built. Biogas is obtained in the biodegradation processes involving the waste from animal husbandry, the manufacture of feed, and municipal waste and is formed in enormous amounts—0.5 nm^3† per kilogram of the processed raw material. Fig. 1 shows that the liquid bioprocessing products are utilised as organic fertilisers and biogas, partly used to maintain the biofermenter in the working state, is ejected as waste. Studies on the membrane separation of biogas have been initiated at the Institute of Petrochemical Synthesis of the USSR Academy of Sciences jointly with the Institute of Microbiology of the Academy of Sciences of the Latvian SSR. Preliminary estimates (Table 3) have shown that the membrane purification of biogas will make it possible to obtain a high calorie fuel, freed from hydrogen sulphide locally, for the autonomous provision of energy without any special ecological consequences. Furthermore, it is possible to obtain technical carbon dioxide.

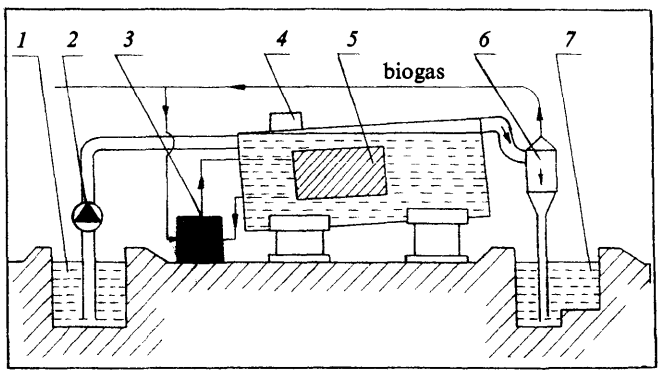


Figure 1. The biogas apparatus (Institute of Microbiology of the Academy of Sciences of the Latvian SSR): (*1*) manure storage compartment; (*2*) pump; (*3*) heat generator; (*4*) service hatch; (*5*) heat exchanger; (*6*) gas–liquid separator; (*7*) organic fertiliser storage compartment.

Table 3. Composition of biogas.

Main components	Initial biogas	After membrane purification
Methane, %	60	95
Carbon dioxide, %	40	5
Accompanying gases (H_2S, H_2, etc.), %	Up to 1	—

The heat generation by the initial biogas and the biogas after membrane purification is indicated below:

	Initial biogas	After membrane purification
Heat generation	50000 kcal nm^{-3}†	8500 kcal nm^{-3}†
	5.8 kW h nm^{-3}†	9.9 kW h nm^{-3}†

*The unit of volume is probably m^3, not nm^3 (Ed. of Translation).

One of the important ecological problems which it will be essential to solve in the next few years with the aid of membrane separation methods is that of reducing the amount of organic solvent vapours or the vapours of petroleum products ejected as waste in the form of mixtures with air. Here a typical source of pollution is not large-scale chemical plants but a multiplicity of small and medium sources—storage depots for motor fuel and filling stations, car body painting workshops in the automobile industry, furnaces for the preparation of sand moulds, etc. In the scheme applied by the Mercedes Company (Federal Republic of Germany), the organic solvent vapours are not only removed from the gaseous medium in such chambers but are also extracted for subsequent use.

Membranes based on cross-linked elastomers are usually employed for processes of this kind. For example, the separation of chloromethanes (methylene chloride, chloroform, and carbon tetrachloride) from nitrogen can be achieved with the aid of membranes based on polychloroprene rubber and its copolymers as a result of the high selectivity of the vapours in relation to nitrogen. The selectivity for gas-separating membranes usually amounts to several tens. As can be seen in Fig. 2, higher selectivities are achieved in this instance, which is extremely important since the typical concentrations of the impurities isolated from air are low.

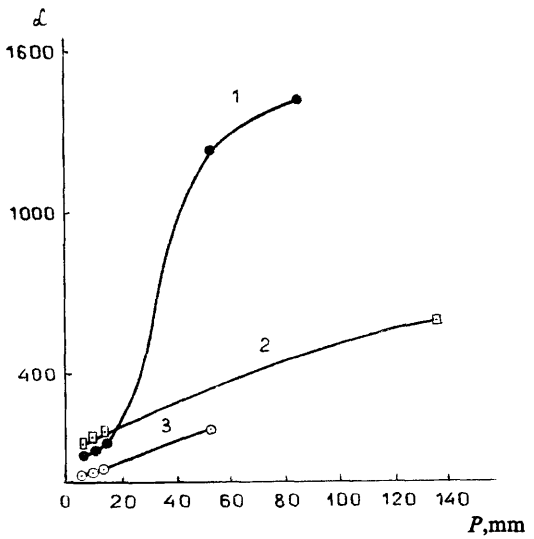


Figure 2. Dependence of the selectivity α (the ratio of the permeability of the organic solvent vapour to the permeability of nitrogen) in the separation of solvent vapours from nitrogen on the partial pressure of the vapour: (*1*) $CHCl_3$; (*2*) CH_2Cl_2; (*3*) CCl_4.

The development of membrane purification methods for gases in order to remove harmful impurities now requires the creation of highly selective and highly permeable membranes with the aid of which it would be possible to solve also the problem of the removal of acid gases from air mixtures.

As an example of the second aspect of the application of membrane processes for ecological purposes, one may consider the oxo synthesis process, i.e. the preparation of secondary alcohols and carbonyl compounds in reactions with participation of synthesis gas. In particular, in the manufacture of butyl alcohols from 2-ethylhexanol, whose output in the USSR amounts to hundreds of thousands of tonnes, the $H_2:CO = 1:1$ synthesis gas is used. On the other hand, in the steam conversion [water gas] reactions, the $H_2:CO = 3:1$ synthesis gas is obtained. Therefore, in order to obtain the synthesis gas with the required composition, one has to apply the complex technology of the copper–ammonia extraction of carbon monoxide from the stream with its subsequent injection into the initial synthesis gas in order to obtain a mixture having the required composition, for example, in the current manufacture of butyl alcohols by the "Perm'nefteorgsintez" Industrial Association.

Part of the gas resulting from the steam conversion of methane (with the composition $H_2:CO = 3:1$) is directed to the carbon monoxide isolation unit with the aid of the copper–ammonia purification. According to the specification, there should be no losses of the copper–ammonia solution, but in reality they occur and are not small. In only one industrial manufacture of the synthesis gas by the "Perm'nefteorgsintez" Industrial Association they amount to 15 tonnes annually when recalculated as metallic copper, i.e. one is dealing with waste comprising a highly toxic metal. Furthermore, ammonia compounds forming part of the composition of the copper–ammonia complex also have an ecologically harmful effect. The replacement of the absorption purification by the membrane process will not only greatly simplify the technological scheme of the process (here there is a possibility of both single- and two-stage versions with intermediate compression of the process product—hydrogen) but also fully eliminates the harmful stage involving washing with the copper–ammonia solution. Bearing in mind that similar and larger plants exist also at other sites (Angarsk, Salavat), the development of a membrane process for controlling the composition of the synthesis gas, which is now being initiated at the Topchiev Institute of Petrochemical Synthesis of the USSR Academy of Sciences in collaboration with the All-Union Institute of Petrochemical Processes, can be important both as regards the community and the protection of the environment.

As regards the third field of application of membranes, nowadays this can concern devices for the preparation of air enriched in oxygen and for the intensification of various biopurification processes. The manufacture of gas-separating devices for the enrichment of air in oxygen based on the Soviet PVTMS gas-separating membrane, the first of its kind in the world, has been initiated in the USSR (Table 4). The "Kriogenmash" Scientific-Industrial Association manufactures also MVK [MAO?—membrane air–oxygen] apparatus of this kind with a productivity of 12.5 to 300 nm^3 of air per hour, the air being enriched in oxygen up to 35%. Such autonomous sources of oxygen are designed to increase the efficiency of the aerobic biopurification of waste; they improve the parameters of other oxidation processes.

One can also imagine that membrane gas-separating devices can play a definite role in the creation of ecologically clean internal combustion engines. Estimates have shown that for this purpose it is necessary to ensure, under room conditions, streams with a flow rate amounting to tens of cubic metres per hour with an oxygen concentration up to 30%. The existing industrial membranes do not possess such capacities. Among laboratory specimens, the greatest hopes are concentrated on polytrimethylsilylpropyne which occupies an unusually high place even in the leading group of organosilicon polymeric membrane materials. Table 5 shows that its permeability is higher by an order of magnitude than the permeabilities of other

materials. If the problem of the manufacture of such a membrane can be solved, then, apart from improving the technical-economical parameters of the operation of the engine, by increasing the oxygen content and reducing the nitrogen level in the air mixture it will be possible also to reduce the ejection into the surrounding atmosphere of the combustion products in the form of hydrocarbons, nitrogen oxides, and solid carbon. The same situation arises also in fuel–energy plants.

Table 4. Membrane gas-separating devices of the MVK series designed for the preparation of air enriched in oxygen directly from the atmosphere.

Principal characteristics	MVK 0.0125	MVK 0.025	MVK 0.3
Productivity, $nm^3 h^{-1}$*	12.5	25.0	300
O_2 concentration, %, not less than	35	35	35
Specific energy consumption, kW h m^{-3}	0.35	0.25	0.14
Starting time, min	1–2	1–2	2–3

*Probably $m^3 h^{-1}$ (Ed. of Translation).

Table 5. Gas permeability coefficients (P) for organosilicon polymers.

Polymer	$10^9 P$, cm^3 cm $cm^{-2} s^{-1}$ $cmHg^{-1}$			
	hydrogen	methane	oxygen	nitrogen
Polyvinyltrimethylsilane	20	1.8	4.4	1.1
Polydimethylsiloxane	65	95	60	28
Polytrimethylsilylpropyne:				
Japan Institute of Petrochemical	690	720	400	200
Synthesis of the USSR Academy of Sciences	700	–	590	280

Thus the possibilities of ecologically clean membrane gas separation processes are associated primarily with the creation of new polymeric materials and membranes with an exceptionally high productivity and selectivity and also with the creation of membrane methods and devices in which the membrane would play not only the role of a separating element but would also be actively involved in the chemical reactions of the substances, i.e. would play the role of a membrane reactor.

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Chemical aspects of a circulating water supply

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One of the most important ecological problems is that of water. Using water from various natural sources in enormous amounts, the human population partly wastes it by evaporation but most of it is returned to nature in the liquid but contaminated form. In the USSR the overall water resources amount on average to 4500 km^3 per year (4/5 corresponds to surface waters and 1/5 to subsoil waters). It is believed that a little more than 110 km^3 of water can be used annually for industrial and agricultural needs and for utilities without harming the water balance in the country. The industrial consumption of water in the USSR runs to many tens of cubic kilometres (from 40 to 60 km^3 according to different data). Approximately the same amount of water is consumed domestically by the population. The manufacture of one tonne of nickel requires on average 800–850 tonnes of water. The bleaching of 1 tonne of cotton requires 280 tonnes of water. One tonne of caustic soda requires 250–300 tonnes of water, etc. Naturally, even in related undertakings, these consumptions differ markedly. Nevertheless they are very large. A similar situation has been observed also in other industrially developed countries. For this reason, the saving of water and the fight against the exhaustion of the water resources of our planet and the contamination of water have now become one of the most important problems facing humanity.

One of the aspects of the solution of this problem involves the conversion of industrial undertakings and heating systems to a circulating water supply. Trends of this kind are characteristic of many branches of industry, but they are perhaps most characteristic of ferrous metallurgy—a large consumer of water.

The water economy in metallurgical undertakings has developed rapidly during the last decades towards the creation of a circulating water supply system.

More than one thousand circulating water supply systems have now been created in the undertakings of the Ministry of Ferrous Metallurgy of the USSR; the fraction of the circulating water supply in the overall water consumption of this branch of industry has exceeded 85%.

The conversion of the water economy of any industry to circulating schemes leads to a gradual impairment of the quality of water in the systems. As a result of the repeated employment of limited volumes of water (with a necessary external supply to make good the losses) in such systems, salts accumulate and dense salt deposits are formed on the equipment.

The formation of salt deposits in circulating water supply systems is now occurring on a wide scale. Industrial undertakings suffer annual additional costs and losses running altogether to several hundreds of millions of roubles. The removal of part of the circulating water to water reservoirs in order to reduce the content of sparingly soluble salts and thus diminish the rate of formation of deposits is used as a palliative solution. It is then necessary to