effective extraction of surfactants from spent waters. The polymeric complexes isolated under these conditions are in their turn highly effective flocculants capable of decomposing simultaneously mineral dispersions and emulsions of organic substances. This has been demonstrated in experiments on the purification of spent waters in the rolling mills of the Moscow "Serp i molot" (Hammer and sickle) factory.

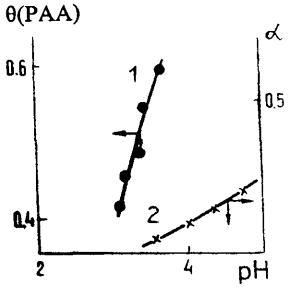


Figure 4. Dependence of the degree of reaction θ between equimolar amounts of polyacrylic acid and dodecyltrimethylammonium bromide (DDTMAB) (curve *1*) (polyacrylic acid and DDTMAB concentrations 0.03 M) on the pH; dependence of the degree of dissociation α of polyacrylic acid (curve *2*) on the pH; c_{NaOH} = 0.1 M; *1*, 20 °C.

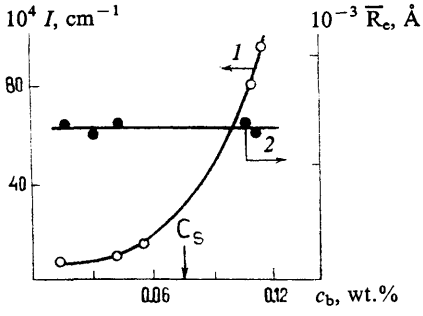


Figure 5. Dependence of the integral intensity of the scattered light *I* (curve *1*) and of the microemulsion drop size ($\bar{R}_e$) (curve *2*) on the amount of emulsified benzene (c_b); composition of the polyelectrolyte complex [PMANa]/[DDTMAB] = 0.2; [PMANa] = 0.03 M; [DDTMAB] = 0.03 M; pH 5.7; t = 20 °C.

The diphilic surfactant ions in the particles of such polymeric complexes are segregated into intramolecular micelles whose size and morphology are determined by the composition of the polymeric complex and the degree of polymerisation of the linear polyelectrolyte. By virtue of the presence of the intramolecular micellar phase, the polyelectrolyte–surfactant polymeric complexes effectively solubilise organic substances which are sparingly soluble in aqueous media, with formation of thermodynamically stable microemulsions of the "oil–water" type. Fig. 5 presents the dependence of the integral intensity of scattered light (curve *1*) and the drop size of microemulsions (curve *2*) on the amount of emulsified benzene. Eviently the size of the drops of the benzene microemulsion in water, stabilised by the complex of sodium polymethacrylate (PMANa) and the surfactant, is independent of the amount of emulsified benzene, while the integral light scattering intensity increases with increase in the amount of emulsified hydrocarbon. It is noteworthy that microemulsions are formed at a hydrocarbon concentration appreciably lower than that of the saturated solution of the hydrocarbon in water (c_s). This means that the drops of the microemulsion consist of a solution in the hydrocarbon of fragments of the polymeric acid bound to the aliphatic groups of the surfactant. The microemulsion particles can be readily separated from the aqueous medium, for example, by adding small amounts of polycations to the system. Thus the polymeric complexes of linear polyelectrolytes with micelle forming surfactants can be used to extract sparingly soluble organic compounds from aqueous media.

Polyelectrolytes have been used successfully also for the extraction of metal ions from aqueous media. Cross-linked polymers, capable of forming complexes with transition metal ions, including heavy metals, are widely used for this purpose. It has been found that the degree and rate of extraction of the metal can be increased by an order of magnitude by using a simple but effective method of "adjusting" the polymeric sorbent to a particular ion. This procedure consists in the fixation of the optimum conformations of the sections of the chains which arise in the polymer-metal complex formed by the linear polyelectrolyte. The complex is then cross-linked. The resulting complex-forming cross-linked polymer "remembers" the optimum structure and in subsequent cycles behave as an "adjusted" highly effective polymeric sorbent.

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New metal- and carbon-containing catalysts for the catalytic removal of harmful impurities from industrial gaseous waste

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The intensification of economic activity has led in recent years to dangerous ecological complications in many regions of our country. Emission into the atmosphere of gaseous waste comprising nitrogen and carbon oxides, carbon disulphide, organic sulphides, hydrogen cyanide, ammonia, and acetylene, which are present in the industrial waste from chemical, petrochemical, gas, and metallurgical industries, in automobile exhausts, in the exhausts from thermal power stations, etc., has given rise to especially great fears.

The incorporation in the processing treatment and the increase in the degree of utilisation of new types of petroleum, gas condensites, and accompanying gases with a high content of hydrogen sulphide and mercaptants are characteristic of the petroleum processing and gas industries in the USSR. For example,

promising petroleum deposits (Tengiz, Zhanazholsk) and gas condensate deposits (Karachanak, Astrakhan, and Orenburg deposits and the adjoining petroleum deposits), characterised by great depths of deposition (3500–5500 m), high pressure at the outlet from the well (50–90 MPa) and an elevated temperature (80–125 °C) as well as a high gas factor (600–900 m^3 $tonne^{-1}$), contain between 5 and 30 wt.% of hydrogen sulphide and 2–15 wt.% of carbon dioxide together with methanethiol, carbon disulphide, and other harmful substances.

The effluent and blast gases in the majority of chemical industries, coke-chemical factories, and other industrial objects also contain considerable concentrations of impurities comprising carbon disulphide, mercaptans, nitrogen oxides, etc. The existing methods of extraction, storage, transport, and processing do not ensure the maintenance of an ecologically safe situation in regions where these products are extracted and processed.

The exhaust gases from internal combustion engines and thermoelectric power stations also make a considerable contribution to the contamination of large cities, especially Moscow, by gases. Nitrogen oxides, formed on combustion of diesel fuel, masoute, and especially natural gas constitute a specially great risk to the health of the population. Thus the change in the fuel used by thermoelectric power stations to natural gas increased almost by an order of magnitude the concentration of nitrogen oxides; their concentration in the centre of Moscow exceeds severalfold the limiting permissible concentration (LPC). It is sufficient to say that one thermal power station with a power output of 300 MW releases annually 194 tonnes of nitrogen oxides, 497 tonnes of sulphur dioxide, and 630 tonnes of carbon monoxide. Polycyclic aromatic hydrocarbons, also formed on incomplete combustion of diesel fuel, are no less dangerous. The limiting permissible concentrations of these compounds are 10^{-6} mg m^{-3}, which is smaller by six orders of magnitude than the concentration of, for example, carbon monoxide and nitrogen oxides.

Several versions of catalytic systems based on precious metals have now been developed abroad; all the automobiles produced must be fitted with them. Unfortunately our country lags appreciably in this respect.

A characteristic feature of the majority of industrial gaseous waste in modern industries is their multicomponent nature, which complicates the solution of the problem of their chemical deactivation by means of a series of different chemical reactions leading to the formation of both harmless and new dangerous substances. For example, when the gas contains components such as sulphur dioxide, hydrogen sulphide, carbon dust (C), and carbon monoxide at the usual process temperatures (200–500 °C), there is a possibility of the occurrence of tens of reactions of this type. Some of them are presented in Table 1.

The picture becomes even more complicated if nitrogen oxides or ammonia are present. In the general case, the situation reduces to the occurrence of a whole sequence of oxidation-reduction reactions, where the compositions of the intermediate and final products are fairly complex or cannot be predicted beforehand. In order to determine the final mixture composition, it is insufficient to know only the initial concentration; the concentrations of the substances are a function of time, local temperature gradients, and the specific features of the action of the catalysts. And yet ecological problems require the virtually complete neutralisation of harmful components; the concentrations of most of them should not exceed tenths or even hundredths of a milligram per cubic metre. A certain polyfunctionality is therefore required from the catalysts employed, including a combination of catalytic and adsorption activities.

Such properties are possessed, in particular, by activated charcoals, but their availability and cost preclude their wide scale employment for the purification of large volumes of industrial gaseous waste.

Table 1. Certain possible reactions of the components of ecologically harmful gas mixtures.

Reaction	Heat change, kcal	Free energy change ΔF^0, kcal mol^{-1}
$2H_2S+SO_2 \rightarrow 2H_2+{}^3/_8S_8$	–	−16.5
$H_2S+{}^1/_2O_2 \rightarrow S+H_2O$	+53	–
$H_2S+{}^3/_2O_2 \rightarrow H_2O+SO_2$	+124	–
$2H_2S+O_2 \rightarrow 2H_2O+S_2$	+106	–
$2H_2S+SO_2 \rightarrow 2H_2O+{}^3/_2S_2$	−11.45	−3.52
$SO_2+2CO \rightarrow 2CO_2+{}^1/_2S_2$	–	−41.09
$CO+{}^1/_2S_2 \rightarrow COS$	–	−17.25
$C+S_2 \rightarrow CS_2$	–	−3.75
$CO_2+C \rightarrow 2CO$	–	ΔH^0=40.79
$2SO_2+2C \rightarrow 2CO_2+S_2$	–	–

We suggested that synthetic metals and carbon-containing catalysts with adsorption and polyfunctional catalytic activities be used for these purposes. They are formed in the catalytic decomposition of hydrocarbons on *d* metals within a certain temperature range. In essence, this phenomenon takes place in virtually each industrial process involving the catalytic processing of a hydrocarbon-containing raw material (catalytic cracking processes, dehydrogenation, reforming, etc.) and is well known as an extremely undesirable process leading to the saturation of catalysts by coke; it entails the loss of their activity and necessitates the regeneration of the catalysts. Systematic studies on this process, carried out by numerous investigators,[1–4] showed that the formation of carbon is a process which takes place in accordance with definite rules and can be fully controlled. The structure of the carbon formed then depends both on the nature of the metal and on the carbon deposition conditions.

A typical dependence of the degree of conversion of hydrocarbons into activated charcoal on temperature passes through an extremum (Fig. 1). The optimum temperatures for a number of oxides (Fig. 1*a*) and hydrocarbons (Fig. 1*b*) are described by general relations in terms of the variables optimum temperature–logarithm of the heat of formation of acetylene from the given raw material (Fig. 2). The optimum temperatures also differ for the same raw material and different metals. We obtained general criterial relations for a multiparameter system of this kind, from which it is possible to find the conditions governing the preparation of the activated charcoal. This makes it possible to predict the process and to control it. It was shown that, for example, in the case of C_8H_{10} the optimum calculated temperature is 757 K, while the experimental temperature is 768 K.

The activated charcoal obtained was studied by various physicochemical methods. The elemental composition, the specific surface, the valence state of the metal, and the X-ray diffraction characteristics of the carbon were investigated.

It was established that metals are present as a rule in the finished catalyst in the zerovalent (reduced) state but have a distorted crystal lattice (Table 2). In the case of iron and cobalt, the formation of carbides and cementides was observed, which does not happen in the case of nickel. The metal particles are distributed throughout the catalyst bed with formation of 100–250 Å clusters. The following structural characteristics were determined from the X-ray diffraction patterns for catalytic carbon: the interplanar spacings d_{002}, the size of the coherent scattering regions (CSR), the size of the pseudocrystallites L_c and L_a, and the diffraction coefficient M characterising the degree of organisation of the carbon atoms to form a graphite-like structure. Table 2 shows that no appreciable correlation is observed between these characteristics and the nickel content in the catalytic carbon.

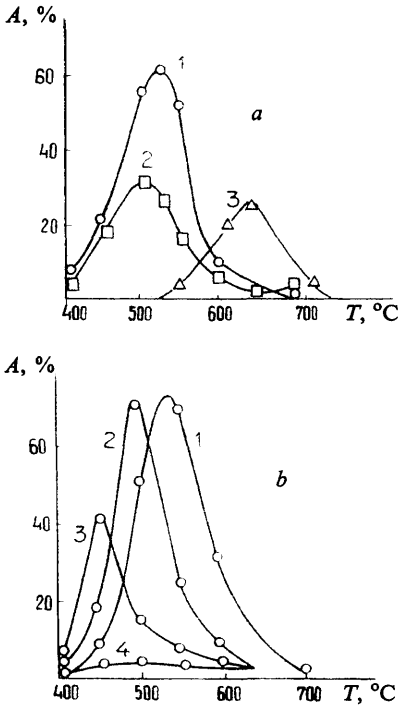


Figure 1. Temperature dependence of the yield of the activated carbon: *a*, for metal oxides (*1*, NiO; *2*, Co_2O_3; *3*, Fe_2O_3); *b*, for hydrocarbons (*1*, C_6H_6; *2*, cyclo-C_6H_{12}; *3*, C_7H_{16}; *4*, $C_3H_5CH_3$).

We shall now consider the principal results obtained in the study of the activities of catalysts both in model mixtures under laboratory conditions using a pulse method and in industrial gaseous waste (Table 3).

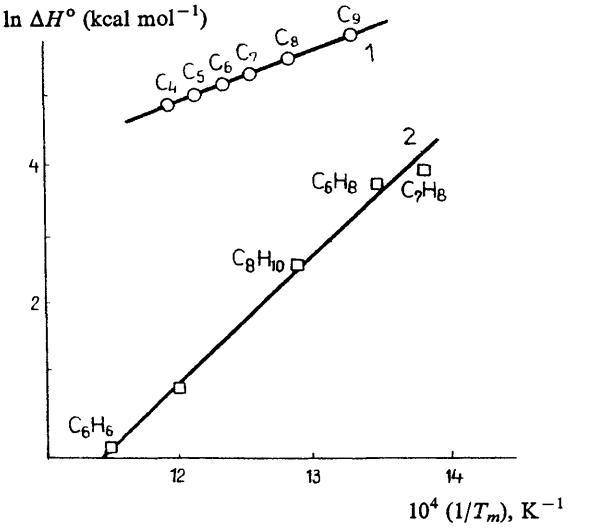


Figure 2. Dependence of the heat of formation of the carbon material ($\Delta H°$) on the optimum process temperature (T_m) for various hydrocarbons: *1*, paraffin; *2*, cyclic (aromatic and unsaturated) hydrocarbons.

Table 2. X-Ray phase analysis of catalytic carbon (DRON-2, Cu K_α line).

c_{Ni}, wt.%	S_{sp}, $m^2 g^{-1}$	d_{002}, Å	L_c, Å	L_a, Å	M, %	Ni	
						CSR, Å	d, Å
0.9	166	3.45	88	94	92.5	–	2.037
2	161	3.46	87	100	91.0	360	2.041
2.8	156	3.41	103	95	92.0	210	2.034
4.5	146	3.41	116	95	87.0	275	2.033
6.0	135	3.42	100	100	91.7	290	2.035
10.0	74	3.40	110	90	82.5	200	2.032
100	–	–	–	–	–	–	2.03

It is also seen from the data presented that, as the hydrocarbon accumulates, the specific adsorption surface increases and the concentration of the metal diminishes, the metal being highly dispersed by the growing carbon.

The specific surface of the catalyst depends on the matrix employed, but it does not as a rule exceed 240–260 $m^2 g^{-1}$ (according to low-temperature nitrogen adsorption data), i.e. is significantly lower than the specific surface of activated charcoal (600–800 $m^2 g^{-1}$). The electron photomicrograph in Fig. 3 shows metal-containing carbon fibres.

Oxygen is absorbed at temperatures in the range 300–350 °C. When the catalyst specimen is treated with oxygen at 300 °C, the evolution of carbon dioxide is not, however, observed. Oxygen is consumed in the oxidation of the nickel reduction centres. At higher temperatures, oxygen is also consumed in the oxidation of the carbon of the catalyst, which results in the evolution of carbon dioxide.

Carbon monoxide is absorbed at temperatures in the range 200–550 °C. Under these conditions, the main reaction product (carbon dioxide) begins to evolve from 300 °C upwards.

Carbon dioxide is absorbed by the catalyst in the temperature range from 20° to 250 °C, the maximum corresponding to 50 °C (1.22 $cm^3\ g^{-1}$). At a temperature above 200 °C, carbon dioxide may be removed by thermal desorption.

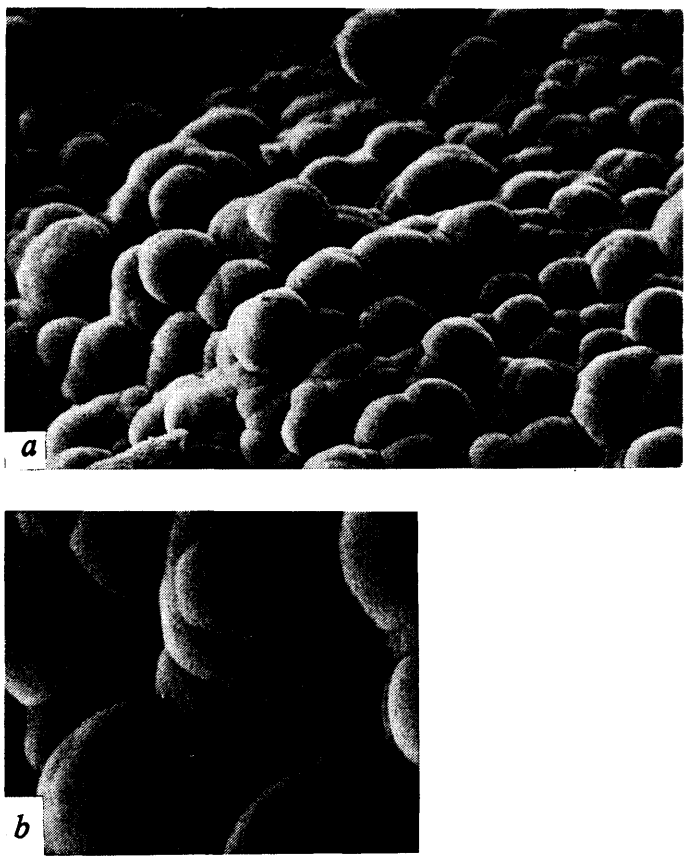


Figure 3. Photomicrographs of the catalyst (on a γ-Al_2O_3 carrier); magnification $\times 350$ (*a*) and 1400 (*b*).

Nitric oxide is absorbed in the temperature range 50–250 °C, the maximum degree of absorption being observed at 150 °C (1.54 $cm^3\ g^{-1}$). Molecular nitrogen is evolved in the same temperature, its amount diminishing with increase in temperature (from 5.0×10^{-2} cm^3 at 50 °C to 0.6×10^{-2} cm^3 at 250 °C). Nitrogen and carbon monoxide and dioxide are evolved on thermal desorption (in the temperature range from 150 °C to 500 °C).

It is of interest to note that the absorption of nitric oxide on activated charcoal does not begin until 200 °C (also with evolution of nitrogen).

In the absence of an oxidant, hydrogen sulphide is poorly adsorbed on the various catalysts tested and does not decompose. In the presence of various oxidants (air, sulphur dioxide), the decomposition of hydrogen sulphide is observed even at room temperature with formation of elemental sulphur (mainly S_8). The amount of adsorbed hydrogen sulphide on the treated catalyst does not exceed 6%. The most active of the catalysts investigated (carbon-saturated γ-Al_2O_3 containing 4.5% of nickel) converted (before breakthrough) 3000 volumes of gas.

Table 3. The activities of catalysts in relation to certain gases.

Gas	Absorption temperature, °C	Chemical reaction temperature, °C	Main product
Oxygen	300–350	>300	Carbon dioxide
Carbon monoxide	200–250	>300	Carbon dioxide
Carbon dioxide	20–250	—	—
Nitric oxide	50–250	>50	Nitrogen
Hydrogen sulphide	20 (pore)	>20*	Sulphur (S_8)
Ammonia	20–450	>20*	Nitrogen
Methane	450–600	>450	Carbon monoxide, carbon dioxide, water
Carbon disulphide, hydrogen cyanide	20	—	Carbon disulphide, hydrogen cyanide

*In the presence of oxidants.

Table 4. Composition of gaseous waste (temperature 350–1100 °C).

Substance	Content, mg m^{-3}
Hydrogen sulphide	360
Sulphur dioxide	60
Carbon monoxide	7.3
Nitrogen oxides	306
Ammonia	197
Benzene	474
Hydrogen cyanide	4
Benzopyrene	0.21
Oxygen and nitrogen	residue

Ammonia is absorbed over the entire experimental temperature range (the maximum is at about 100 °C). Ammonia is an effective reducing agent, which reduces the metal, carbon oxides, and nitrogen oxides. Thermal desorption begins at 450 °C with evolution of nitrogen into the gas phase.

Methane is absorbed at fairly high temperatures (450–600 °C), carbon monoxide and dioxide being evolved into the gas phase. The same products are also formed on thermal desorption. The same temperature range is characteristic of the activity in relation to the methane–nitric oxide mixture.

A catalytic effect was not observed in relation to mercaptans, carbon disulphide, and hydrogen cyanide. Mercaptans, using butanethiol as an example, are not absorbed, while carbon disulphide and hydrogen cyanide remain on the catalyst in the adsorbed form. Aliphatic and aromatic alkyl-substituted hydrocarbons are also effectively adsorbed. The strength of adsorption of hydrogen cyanide is confirmed by the fact that it is desorbed at a temperature above 200 °C. However, these compounds can interact on contact with oxidising gases.

The results obtained in preliminary tests on catalysts in industrial gaseous waste from the Moscow Coke–Gas Factory (MCGF), the Kashirsk Thermoelectric Power Station, and the Cellulose Industry in Krasnoyarsk are presented below. Table 4 gives the composition of the effluent gases from the MCGF.

As a result of the application of the catalyst, hydrogen sulphide, hydrogen cyanide, and nitric oxide are eliminated from the gases (Table 5).

Table 5. Results of tests on new catalytic systems (MCGF).

Source of waste	Ecologically harmful impurity	Catalyst operating conditions		Impurity concentration, mg m^{-1}		Duration of operation before breakthrough	Efficiency of purification, %
		space velocity, h^{-1}	temperature, °C	before purifcation	after purification		
Straight run coke gas	Hydrogen sulphide	300	20	3000	0	312	100.0
Reverse run coke gas	"	470	20	30	0	816	100.0
Straight run coke gas	Hydrogen cyanide, hydrogen	300	20	1000	2.8	1440	99.7
Reverse run coke gas	"	100	20	171	6.0	1440	99.8
	Acetylene	300	200	800	82.7	1440	89.7
	Nitrogen oxides	2000	300	0.21	0.065	1440	69.0
Industrial waste at the MCGF	Ammonia	300	500	1500–78 500	64–28 500	1440	84.0–99.9
Removal of ammonia from aqueous solution by bubbling	"	300	500	134 000	600	1440	96.4
Petrol engine	Nitrogen oxides	12 000	180	1600 ppm	140 ppm	1440	91.0
Stand with UMZ-416 engine	Carbon monoxide	12 000	270	3500 ppm	170 ppm	1440	95.0
Manufacture of viscose	Carbon disulphide	1000	20	1300	50	1	96.1
	"	1000	20	500	9	1	98.2

The advantages of the catalysts described above are as follows:

availability and the possibility of obtaining them directly in the factory, since this requires only a carrier, a hydrocarbon gas, a metal salt, and plant of suitable size and of a relatively simple design;

a lower cost than that of activated charcoal, which makes it possible to organise a large scale industrial production without a large capital expenditure;

the possibility of using spent catalysts, already containing metals, as carriers;

the use of catalysts makes it possible to combine adsorption and catalytic purification processes;

The solution of the problem of the elimination of ecologically harmful impurities from gaseous waste can be reduced (in view of the multifunctional nature of the catalyst) to setting up a balance between oxidative and reductive components. This provides a simple and effective lever for controlling the process, can guarantee the reliability and quality of the purification, and creates conditions for automating the purification processes and the monitoring of the chemical composition of the waste.

The large scale employment of the systems developed requires the creation and organisation of the production of standard apparatus for coating inorganic materials with carbon. At the present time, there exists only laboratory apparatus as well as the plant at the MCGF, which has made it possible to produce one tonne of the catalyst. It is necessary to solve a series of technological problems (in particular, the problem of the additional aerodynamic resistance to the effluent gases) and to develop methods for the regeneration of the catalysts. Furthermore, it is essential to develop apparatus for the rapid analysis of the effluent gases before and after purification, a computer technique, and a module for the automatic control of the purification processes.

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Membrane technology in the resolution of nature conservancy problems

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1. The potential of membrane technology and certain examples

In future membrane technology could provide the basis for resolving a number of ecological problems in many branches of industry and agriculture. Practical experience throughout the world has highlighted examples of how membrane technology may be used on the industrial scale in order to resolve ecological problems.

First of all there is the project in the USA now in its final stages in which the salinity of the Colorado river has been reduced from 1.5 g^{-1} to approximately 0.7 g^{-1} (i.e. in regard to salt content the water has been converted to drinking water). A similar water processing facility is now under construction in the town of Hume (Arizona state) close to the border with Mexico. In this case part of the river discharge will be channelled through the desalination plant where blocks of membrane assemblies for reverse osmosis are located and have an operating efficiency of 400 thousand cubic metres per day. Under these conditions the solvent (water) is forced through the membranes in the presence of a high osmotic pressure (the operating pressure is usually approximately 3–5 MPa) while salts