

that are equal *ca.* to 84 000 Nm³ per year. However, the expenses related to methane losses are compensated by the lower costs of materials consumption. The chemical method is more energy-consuming, uses more reagents like potassium carbonate, activator (DEA) and corrosion inhibitor (KVO₃). In this method, in some parts of installation waste heat can be utilized, that reduces the total energy consumption.

In Table 2, the consumption of energy and reagents is presented. The energy consumption for absorption is reduced by waste energy utilized in some parts of installation.

The investment costs of both methods are listed in Table 3. The tentative cost evaluation showed

Table 3. Economy of two processes: absorption and membrane separation for methane enrichment – a comparison.

Type of costs	Absorption method	Membrane method
Capital costs [PLN]	390 800	354 000
Operational costs [PLN]:	140 582	124 866
- electric energy	3 326	99 666
- thermal energy	21 000	-
- gas losses	-	25 200
- K ₂ CO ₃ loss	71 400	-
- DEA activator loss	21 336	-
- corrosion inhibitor KVO ₃ loss	23 520	-

that the membrane method is more economical than the absorption method. Both capital and operational costs are lower for the membrane process than for chemical absorption. Additionally,

the membrane installation is simple, compact and does not need complex control equipment like chemical methods. Despite of high costs of the membrane modules for gas separation, the total capital costs of the membrane installation are lower than for the Benfield installation.

Comparison of the operational costs is also favourable for membrane permeation. Even though the membrane method consumes much energy for gas compression, it does not use the expensive reagents, which are necessary for chemical process.

The work proved that the absorption method can be superseded by membrane separation. Thanks to the development of material science that produces modern high selective materials and new achievements in process engineering, separation of gaseous components of biogas are reliable. Both selectivity and efficiency of membranes are sufficient to produce gas of appropriate parameters of standard gas GZ-50.

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STUDY OF BOUNDARY-LAYER PHENOMENA IN MEMBRANE PROCESSES

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Pressure-driven membrane filtration is an important process for separation of colloids and particulate matter from liquid suspensions in many fields of engineering and applied science. There are many examples of application of pressure-driven membrane processes in nuclear technology. Such processes like reverse osmosis, ultrafiltration or microfiltration can be used for liquid radioactive waste processing, cleaning reactor waters, boric acid recovery and separation of isotopes. The pressure-driven membrane filtration process can operate at either cross-flow or dead-end flow mode. In case of dead-end filtration the resistance increases with formation of the cake on the membrane surface, while in cross-flow process the deposition continues until the cake adhesion is balanced by shearing forces of the liquid passing over the membrane. It

is important to keep appropriate hydrodynamic conditions in the apparatus that avoid continuous building-up of the cake layer which results in increase of the resistance and reduction of the permeate flux. The term of concentration polarization describes the tendency of the solute to accumulate in the membrane-liquid interface. It is important to suppress the concentration polarization by adjusting the flux on the level that avoid the boundary level development or by promoting the turbulence by all available means. For understanding of permeate flux decline mechanisms and predicting of the permeate flow rate, the development of mathematical models and tools for simulations and optimization are of great importance.

The hybrid membrane process for removal of cobalt ions, the main components of the liquid

radioactive wastes produced in Poland, was run in the ultrafiltration unit equipped with a membrane contactor with a central rotor. Helical Couette-Taylor flow was expected to promote the turbulence and vortices in the apparatus that resulted in good transport parameters. Before filtration,

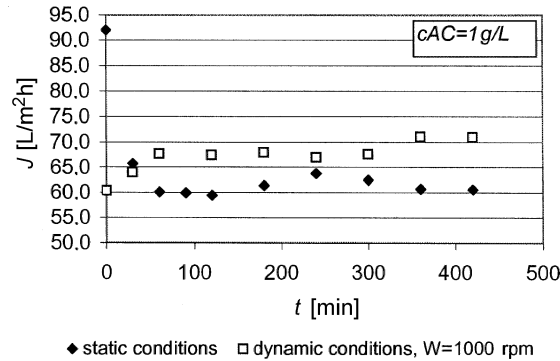


Fig. 1. Permeate flux vs. time. Cobalt removal in hybrid process: sorption on activated carbon (AC)-ultrafiltration.

cobalt ions were complexed by soluble chelating polymers like polyacrylic acid derivatives or adsorbed on activated carbon seeds dispersed in the solution. In both cases the improvement of filtration conditions and increase of permeate flux through the membrane were observed when dynamic conditions were applied (Figs.1-2). There

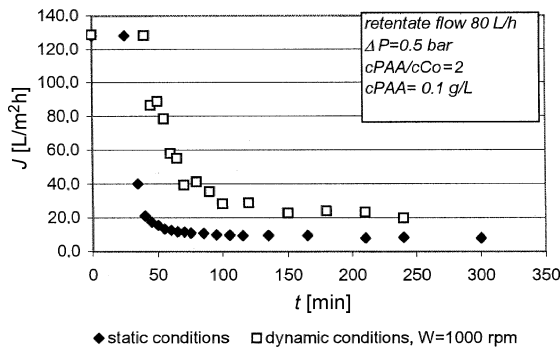


Fig. 2. Permeate flux vs. time. Cobalt removal in hybrid process: complexation by polyacrylic acid (PAA)-ultrafiltration.

was evidence that by promoting the turbulence the resistance of boundary layer and the resistance of the deposit accumulated on the membrane surface were reduced. Permeate flux, J_v , can be expressed as a function of total membrane-cake resistance by the equation:

$$J_v = \frac{\Delta P}{\mu(R_m + R_\delta)} \quad (1)$$

where: ΔP – transmembrane pressure, μ – viscosity of the liquid.

Membrane resistance, R_m , was estimated from water permeability and cake layer resistance R_δ – from the total resistance determined in experiments. On the other hand, permeate flux can be described by the relationship analogical to the equation of the filtration through the sediments:

$$J_v = \frac{\Delta P K}{\mu \delta} \quad (2)$$

where: K – cake permeability, δ – thickness of the cake layer.

From comparison of equations (1) and (2), the thickness of the residual deposit layer can be estimated. The cake thickness determined for different process conditions, assuming $K=10^{-17} \text{ m}^2$, was in a 0.035-0.186 mm range for dynamic conditions. The thickness showed a marked influence of rotation: the δ values decreased with increasing rotation frequency in the helical-flow membrane apparatus. The influence of rotation on the separation efficiency was not observed. In experimental conditions at rotation frequency $W=1000\text{-}1500$ rpm and for ion to polymer concentration ratio $C_{\text{Co}^{2+}}/C_{\text{polymer}}=1/4$, the retention factors higher than 90% were achieved.

The models for simulation and optimization of cross-flow filtration developed from theory of concentration polarization and response surface methodology (RSM) were elaborated. The regression analysis in order to find empirical models for fitting the experimental data of flux decline was employed. The models were determined by minimization of the residual variance S_{res}^2 :

$$S_{\text{res}}^2 = \frac{1}{n-2} \sum_{j=1}^n (J(t_j) - J_j^{\text{exper}})^2 \rightarrow \min \quad (3)$$

The experimental data of the kinetics of flux decline were fitted well by polynomial equation of type:

$$J(t) = a_0 + a_1 \sqrt{t} + a_2 t + a_3 t^{-1} + a_4 t^2 + a_5 t^3 \quad (4)$$

Two responses derived from kinetic curves of flux decline were used: the average permeate flux calculated by integration of $J(t)$ function from $t_1=1$ min up to $t_n=180$ min as follows:

$$\langle J \rangle = \frac{1}{t_n - t_1} \int_{t_1}^{t_n} J(t) dt \quad (5)$$

where $J(t)$ means the regression functions determined by regression analysis, and the cumulative flux decline defined as

$$S_{FD} = \sum_{i=2}^n \left(\frac{J(t_1) - J(t_i)}{J(t_1)} \right) \quad (6)$$

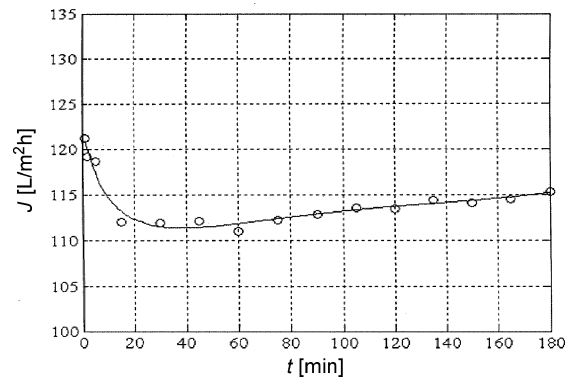


Fig. 3. Permeate flux vs. time for optimal conditions: $\Delta P^*=0.19$ bar, $Q_R^*=54$ L/m³h and $W=2480$ rpm.

The cumulative flux decline defined by equation (6) gives information about all experimental points in flux decline curve for the time interval studied, *i.e.* $1 \text{ min} \leq t \leq 180 \text{ min}$. By means of the multiple linear regression method, the empirical models of cross-flow filtration, which gave the information about the influence of hydrodynamic parameters upon J and S_{FD} were developed. The cumulative flux decline and average permeate flux were used as the objective functions in optimization by the Lagrange multiplier method using MathCAD software. The calculated optimal values in terms of actual operating variables were $\Delta P^* = 0.19 \text{ bar}$, $Q_R^* = 54 \text{ L/m}^2\text{h}$ and $W = 2480 \text{ rpm}$. For these operation con-

ditions, the check out experiment was carried out to determine the permeate flux *vs.* time (Fig.3). The initial flux decline was observed in the time interval $1 \text{ min} \leq t \leq 60 \text{ min}$; after that a slight increase of flux was recognized for $t > 60 \text{ min}$. This means that in optimal operating conditions the vortices created by Taylor flow led to self-cleaning effect of the membrane surface for $t > 60 \text{ min}$. For all experiments concerning the polymer-assisted cross-flow ultrafiltration process carried out in the helical membrane module, the average value of the rejection coefficient was 91.54% with a standard deviation of 4.06%.

A STUDY OF STABLE ISOTOPE COMPOSITION IN MILK

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Isotope ratio mass spectrometry (IRMS) methods play a very important role in food authenticity and origin control. The measurements of bioelements (hydrogen, nitrogen, carbon, oxygen, and sulfur) composition provide a very sensitive tool to food control. The isotopic methods of origin and authenticity control were recently implemented in European Union for wine, juice, and honey.

The aim of our study is to explore the relationship between isotopic composition of milk and its origin (regional, seasonal). The stable isotope composition of food is strictly connected with environmental conditions (climate, geographical position and included pollutants).

The bases for this study are isotopic effects (biological, physical and chemical) which are responsible for different isotopic composition in nature: soil, air and water. The effect of differentiation of isotope composition is connected with different composition of cow diet (maize, grass *etc.*) and different composition of drinking water for cows [1-3]. Seasonal and regional variations of cow diet composition cause seasonal and regional variations of isotopic composition of milk and finally dairy products (Table).

Correlation between the stable isotope composition $^{18}\text{O}/^{16}\text{O}$, $^{13}\text{C}/^{12}\text{C}$, $^{15}\text{N}/^{14}\text{N}$ and δD in milk components was analyzed. The variability of the parameters related to environmental factors like: geology, climate and anthropogenic factors was studied (Fig.).

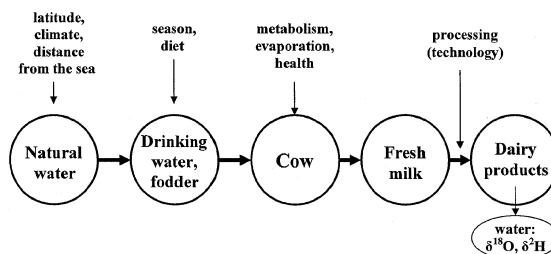


Fig. Factors determining the water isotopic composition of dairy products – a schematic way from the farm to the consumer.

Finally, on the basis of the collected results a map of isotopic parameters distribution will be drawn. The information about the relation between the isotopic compositions and the regional and seasonal factors will be an important research

Table. Chemical components of milk and their important isotopic composition.

Chemical component	Element	Isotope ratio	Source	Critical factors
Water	oxygen	$^{18}\text{O}/^{16}\text{O}$	drinking water, fodder (grass, maize, beet, hay)	hydrogeology, geographical origin
	hydrogen	$^2\text{H}/^1\text{H}$		plants: C3, C4
Casein, lactose, fat, minerals	carbon	$^{13}\text{C}/^{12}\text{C}$		fertilizers: organic or synthetic
	nitrogen	$^{15}\text{N}/^{14}\text{N}$		geology, air pollutants
	sulfur	$^{34}\text{S}/^{32}\text{S}$		

In the frame of the project, many samples of milk and dairy products from main regions of milk production were gained. The collected samples were measured by the use of IRMS DELTA_{plus} (Finnigan, Germany), connected with peripheral units as: GasBench, H/Device and Elementar Analyzer (ThermoFinnigan).

result of this project. In the future, on the data base of authentic value of stable isotope composition, the method for origin control of milk and dairy products will be proposed.

The study was supported by the Polish Ministry of Science and Higher Education in the frame of project No. 2P06T03928.