NUKLEONIKA 2006;51(Supplement 1):S101–S111

Membrane processes for environmental protection: applications in nuclear technology

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Abstract Membrane processes are considered as potential methods useful in clean technologies that minimize the use of raw materials, rationalize energy consumption and reduce waste production. They are capable to solve many environmental problems, among them problems related to nuclear technology field. Membrane processes have been already applied for liquid radioactive waste processing in many nuclear centres around the world. Reverse osmosis (RO) was implemented at the Institute of Atomic Energy (IAE) at Świerk for liquid low-level radioactive waste concentration. A 3-stage RO plant supplements the existing waste processing system based on an evaporator giving the possibility of initial concentration of liquid waste or final polishing of the condensate after evaporation. Intensive studies on ultrafiltration (UF) enhanced by sorption on inorganic sorbents or complexation with chelating polymers were carried out. Ceramic membranes made of alumina, titania and zirconia were used in the experiments. Such membranes show a high chemical, temperature and radiation resistance. Thermal process, namely membrane distillation with the use of resistant porous membranes from PTFE was proposed and tested for radioactive waste concentration. The results collected in laboratory and pilot plant experiments allowed to consider the process usable for small installations operated with utilization of cheap energy sources or waste heat. Other methods like liquid membranes and electric processes with ion-exchange membranes as possible applications in nuclear industry are under development. Membrane methods were considered as alternative solutions for reclamation of different materials that can be recycled and reused. Some of them allow minimizing the total energy consumption by various energy recovery systems and utilization of cheap energy sources.

Key words clean technologies • membrane processes • radioactive waste processing • recycling • reuse

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Received: 14 November 2005

Membranes and membrane processes

Membrane processes with their flexibility, separation efficiency and low-energy consumption can be used for treatment of various process streams. Different driving forces can be applied; apart from the most developed pressure-driven membrane processes, thermal methods proceeded with temperature difference, diffusion processes – with concentration gradient, as well as processes driven by electric or chemical potentials can be considered.

Membrane structure defines membrane functionality and performance. Since relation between the structure and separation properties of the membrane is evident, it is important to know its characteristics as medium pore size, pore size distribution, porosity, free volume or crystallinity. Good performance of the membrane can be achieved with high selectivity and large fluxes. In consequence, the membrane should be characterized by a narrow pore size distribution, high porosity.

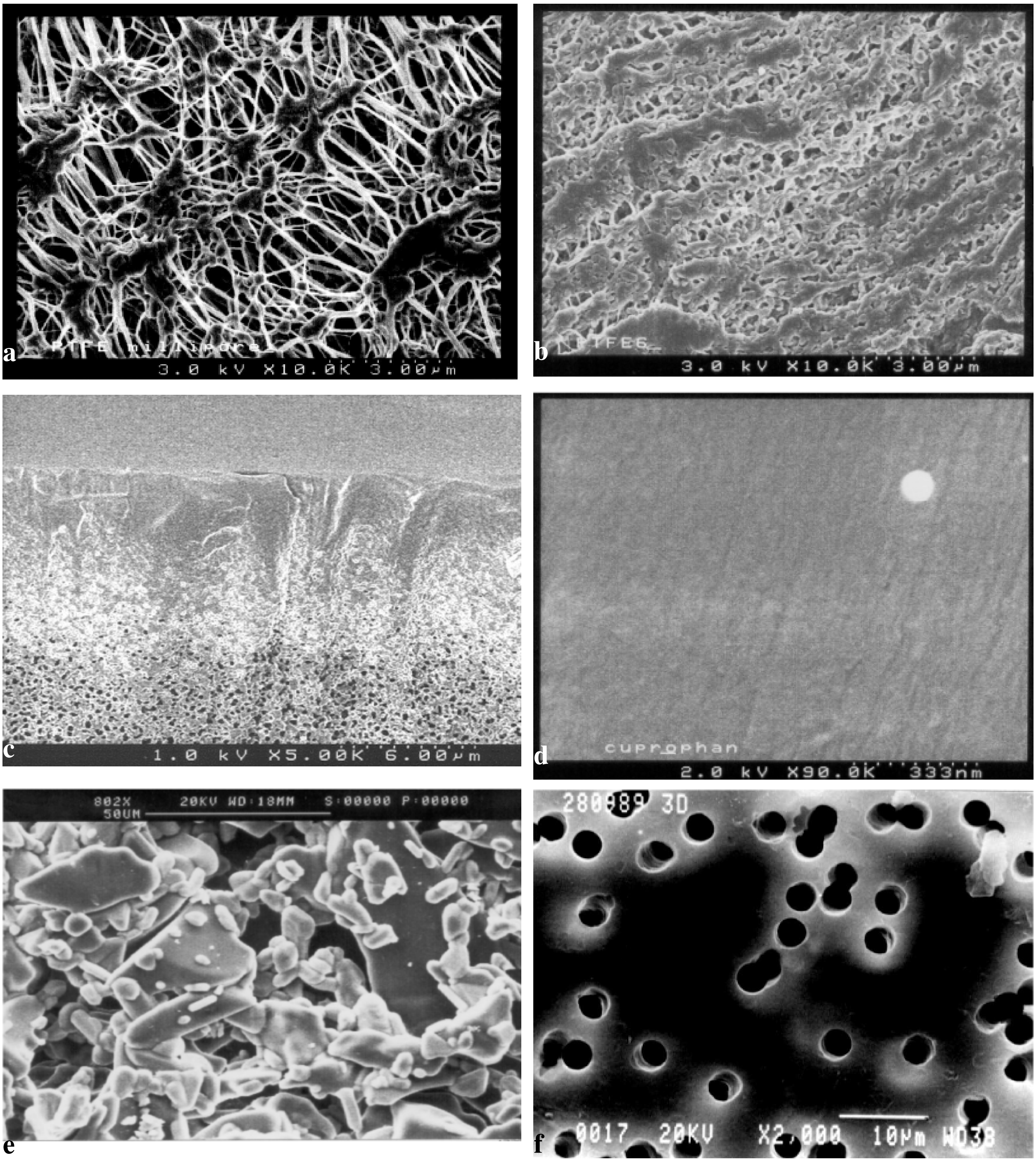

Fig. 1. SEM micrographs of flat-sheet membranes: a – FGLP porous membrane; b – PTFE-Tarflen; c – asymmetric composite membrane; d – cuprophane cellulose dense membrane; e – porous ceramic membrane (electron microscope S-4500 HITACHI, Ecole National Superiere de Chemie, Montpellier); f – estrofol track membrane (electron scanning microscope TESLA BS 340, INCT).

The images of different membranes used at the Institute of Nuclear Chemistry and Technology (INCT) for different purposes and various applications in nuclear technology field (separation of isotopes, radioactive waste processing, production of pure water for power applications) are presented in Fig. 1. For liquid radioactive waste processing, mainly porous, asymmetric membranes are employed, they are used in pressure-driven processes like MF, UF and RO. In the last process more common are thin-layer composite membranes, which give good separation, as well as reasonably high fluxes. Very important from the radiological point of view is the geometry of membranes.

Clean technologies and environmental applications of membranes

The concept of use of membrane processes for environment conservation is well known for the decades. Every year the world membrane market spreads out and application potential of membrane techniques increases. The main applications of membranes in environmental protection area are as follows: surface water purification, ground water recovery, purification of landfill leachates, wastewater treatment, remediation of contaminated soils, flue gas cleaning, biogas conditioning.

Membrane processes are among those techniques that are considered for potential implementations in clean technologies. The definition of these technologies according to European Commission directive [9] is as follows: "clean technologies are new industrial processes or modifications of existing ones intended to reduce the impact of production activities on the environment, including reducing the use of energy and raw materials". To support this definition the main attributes of clean technologies were precisely formulated: conservation of raw materials, optimization of production processes, rational use of raw materials, rational use of energy, rational use of water, disposal or recycling of unavoidable waste, accident prevention, risk management to prevent major pollution, restoring sites after cessation of activities.

Practically, management of radioactive waste on account of its specificity is close to all those aims. Rational use of raw materials, disposal of the waste, risk evaluation, prevention of accidents and strict rules concerning decommissioning of nuclear facilities from the very beginning of nuclear era were of great importance.

Nuclear industry – processing of liquid radioactive wastes

Radioactive wastes are produced within the fuel cycle. They are also generated during production and application of radioisotopes, as well as during processing of raw materials containing naturally occurring radioactive isotopes. The main sources of such waste are as follows: uranium and thorium mining and milling, nuclear fuel cycle operations (uranium conversion and enrichment, fuel fabrication and spent fuel reprocessing), operation of nuclear power plants, decontamination and decommissioning of nuclear facilities, institutional uses of radioisotopes (medicine, industry, agriculture, research reactors and test facilities).

The wastes produced by all those operations have to be processed before safe storage or disposal.

The management of radioactive waste has to be reached with reasonable cost by use of appropriate technologies. Different methods are used to treat aqueous radioactive wastes, including chemical precipitation, evaporation, ion exchange, as well as less developed other electrochemical methods, solvent extraction, biotechnological processes and membrane methods. Although membrane processes are still considered novel technologies in nuclear industry, many applications are reported in the literature.

By application of membrane processes it is possible to achieve the goals: purification of effluents to the concentration levels enabling safe discharge to the environment, concentration of the radioactive compounds with volume reduction sufficient for solidification, separation and recycling of the valuable components, e.g. boric acid from cooling waters.

Membrane methods for processing of liquid radioactive wastes

Purification strategies

The selection of the process and membranes for purification depends on the origin and characteristics of processed streams and the aims that have to be reached by the treatment. The composition of the wastes, content of toxic substances, which have to be removed, and their limits in discharged effluents have to be taken into account. In purification strategies the following membrane processes can be considered: reverse osmosis with thin-layer composites, nanofiltration with different type of polymeric membranes (1 kD cut off ceramic membranes are also available), ultrafiltration and microfiltration – porous polymeric and inorganic membranes, electrodialysis with ion exchange membranes for separation of ionic substances and charged particles, membrane distillation (MD) – porous polymeric water-repelling membranes, in case of gaseous mixtures gas separation process with dense or porous membranes is applied.

Reverse osmosis

Reverse osmosis is nowadays a mature technology, which has already been applied in many branches of science and industry. It has also been employed on a full scale in many nuclear centres around the world for radioactive waste processing. With its capability of rejection of all contaminants reverse osmosis can replace the evaporation process or ion exchange. Permeate after reverse osmosis can be directly discharged to the environment or recycled as technological water within a nuclear power plant. There is a number of industrial RO applications and facilities in the stage of pilot plants operating for radioactive waste processing.

<u>Case study</u>: Reverse osmosis for liquid low and medium level radioactive wastes processing [6]

The RO method was implemented at the IAE, Department of Radioactive Waste Treatment, at Świerk, which is responsible for the management of all radioactive waste produced in Poland. The IAE collects, treats, conditions, transports and stores the wastes prior the disposal at the central repository at Różan.

Membrane installation constructed at the INCT (Fig. 2), ~ 1 m^3/h of capacity, is composed of three stages of reverse osmosis preceded by pretreatment with polypropylene depth filters. There are two passes for permeate purification and two stages of concentration of retentate. Two types of spiral wound RO modules are used in the installation: SU-720R and desalination-type SU-810 (TORAY). Both types of modules work under a pressure of 20 bar and with salt rejection higher than 99%. The membranes are a cross-linked fully

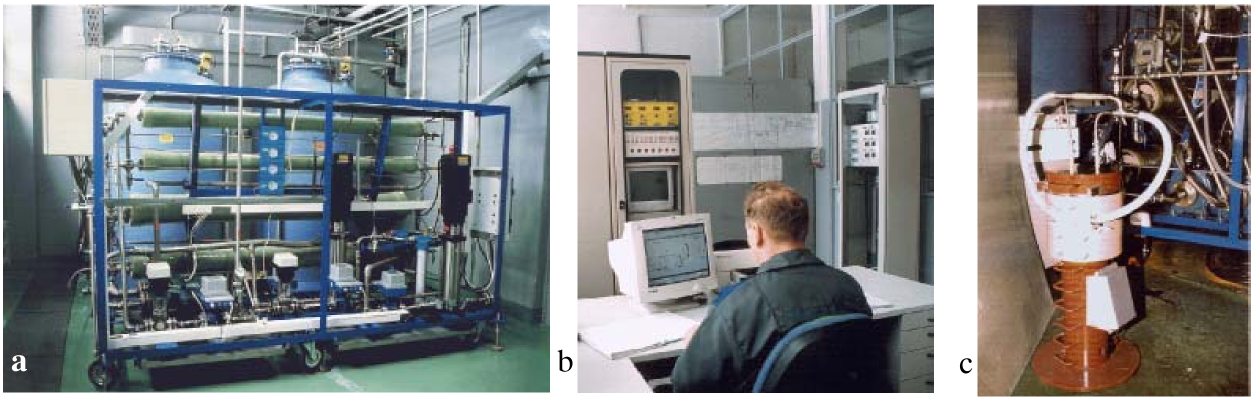

Fig. 2. Reverse osmosis plant for radioactive wastes processing in IAE, Świerk. a – General plant view; b – control room; c – permeate radioactivity measurement probe.

aromatic polyamide composite. Model SU-720R modules connected in series placed in one housing form two stages of purification. The final concentration stage is composed of two housings in parallel, two model SU-810 (TORAY) modules in each vessel.

Liquid radioactive wastes are directed from the central storage tank to an 8 m^2 – feed reservoir. After pretreatment with polypropylene depth filters and injection of an anti-scaling agent, the wastes undergo purification in the first stage of RO. The retentate after this pass is concentrated in the third RO stage. This concentrate can be directly stabilized with concrete if the concentration of the total solute is appropriate (~ 250 g/dm^3) and its specific radioactivity does not exceed the limits for that kind of waste. If the concentration is not sufficient, the further treatment takes place in the evaporator. The permeate from the first and third stages is directed to a permeate reservoir before the second RO unit. The product from the membrane installation (permeate from the second stage) after control of its specific activity and salinity can be discharged to the communal sewage.

The installation is integrated with an evaporator; it can treat the wastes before evaporation improving the process economy by a decrease of total volume of the wastes treated in the evaporation process. The other function of the RO plant is final polishing of the condensate after the evaporator.

Nanofiltration

Nanofiltration (NF) with membrane pores within the range 0.001–0.01 μm is placed between reverse osmosis and ultrafiltration, and since then sometimes considered as "loose reverse osmosis". Typical operating pressures for NF are 0.3–1.4 MPa. The process allows separating monovalent ions from multivalent ions, which are retained by an NF membrane. This can be used for the separation of organic compounds of moderate molecular weight from solutions of monovalent ions. Very well known application in a nuclear industry is boric acid recovery from contaminated cooling water in nuclear reactor. There are some examples of nanofiltration applications and studies done with the aim of implementation in nuclear centres, described in the literature [2, 5, 12].

Ultrafiltration

Ultrafiltration (UF) operates at lower pressures (0.2–1 MPa) than reverse osmosis and with higher permeate fluxes. It uses more porous membranes, pore size of 0.001–0.1 μm. In such a case dissolved compounds pass through the membrane, while colloid and suspended matters are rejected.

In nuclear industry ultrafiltration was applied first of all in the pretreatment stage before reverse osmosis, which needs removal of potential foulants from feed streams. UF can be used separately for removal of all substances, which are present in radioactive waste in the colloidal form, like some actinide compounds, or in the suspended form [3, 14]. Very often UF is combined with precipitation or complexation [7]. Small ions bound by macromolecular chelating agents form complexes, which are easily retained by UF membrane. Such an "enhanced" ultrafiltration becomes an efficient separation process with high decontamination factors, sometimes compared with those obtained by reverse osmosis. Radioactive cations can be removed in the precipitation process forming less soluble particles (carbonates, phosphates, oxalates, ferrocyanides or hydroxides), which are later filtered with UF membrane. These hybrid methods are effectively used in many plants processing alpha bearing radioactive waste streams. Numerous installations are under operation in nuclear centres and many efforts are done to implement ultrafiltration for radioactive wastes processing.

Case study: Liquid radioactive wastes treatment by enhanced UF [19, 20]

The UF plant at the INCT consists of feed tank, membrane module housing, pretreatment polypropylene depth filters, pressure pump TONKAFLO and circulating pump Grundfos. The installation is equipped with a system of visualization and data recording, consisted of electronic pressure difference converters, converters of pressure and temperature, flowmeters, conductivity meters, pH-meter, programmed 8-channel indicator Eftronik V, collecting the data from the object and visualizing software for acquisition and processing the data, elaborated for installation needs on the basis of INTOUCH 7.0 software (USA, Wonderware Corporation) installed in a computer. The plant is equipped with Sunflower CéRAM INSIDE® (23-8-1178) 23-channel ceramic module, 8 kD cut-off.

The process is conducted in a cross-flow mode, the pressure in the system being 0.25–0.5 MPa. In that pressure range the permeate flux of water vary from 26 to 85 l/m^{2}h. All process parameters are recorded with data acquisition system; periodically, the samples of permeate and retentate are collected for chemical analysis.

For removal of radioactive small ions, ultrafiltration can be combined with complexation to enlarge the size of separated molecules. As complexing agents, the following soluble polymers are used: Instar AS (ICSO Chemical Production, Poland) containing macromolecular acrylamid and sodium acrylate copolymer, polyethylenimine (PEI) (Sigma-Aldrich Chemie GmbH), polyacrylic acid of different molecular weight M_w, and sodium or potassium polyacrylates – (NaPAA) (Aldrich Chemical Company, Inc.). The ratio of the polymer concentration to the concentration of the metal ion was selected in the experiments. The ratio changed in the range of 1:1 – 20:1. Caesium isotopes are bound by cyanoferrates of transition metals that resulted in the high decontamination factors. A complexing agent is added to the feed solution before filtration and the solution is mixed for 1–2 h and then seasoned for several hours to establish equilibrium (stable activity of permeate). In time of seasoning, the pH is fixed at the required level, selected in the laboratory experiments.

An example of results of the treatment of original radioactive waste sample is shown in Fig. 3. The sample consisted of the radioisotopes: ^{60}Co, ^{65}Zn, ^{133}Ba, ^{134}Cs, ^{137}Cs, ^{152}Eu and ^{241}Am. Application of sole ultrafiltration gave small decontamination factors, as the main components of the waste were small ions that easily passed through the UF membrane. To enhance retention, ultrafiltration was combined with complexation. Figure 3 presents the concentration of each radioisotope present in the waste in permeate after UF/complexation hybrid process: P1 – permeate treated by complexation with 1 g/l of NaPAA, P2 – permeate after complexation with 3 g/l NaPAA and P4 – after the treatment with cobalt hexacyanoferrate (CoCF) and INSTAR AS. The radiochemical analysis of P1 sample showed a decrease of concentration of almost all radioactive components; only caesium isotopes were retained in lesser amount. They were not complexed by polymers, what was evident also after analysis of P2 sample. The retention of ^{152}Eu was complete. ^{241}Am was removed after the second portion of NaPAA. Caesium isotopes were retained when cyanoferrate was introduced. Due to the high initial ^{65}Zn content, the concentration of this radioisotope in permeate (P4) was relatively high.

Microfiltration

Microfiltration usually operates at pressures up to 0.1 MPa and with high permeate flux. The MF membranes separate bigger particles and macromolecules with a size of 0.1–1 μm. In nuclear technology, the process is used either for pretreatment purposes or for concentration of coarse particles after precipitation process. For high-level radioactive wastes, the ceramic filters are applied, giving for some types of effluents high decontamination and concentration factors.

Pressure-driven membrane processes are very well developed and they have already found their place in nuclear technology. Other membrane processes that do not utilize pressure difference as a driving force, but electric potential, temperature or concentration gradient, are tested for radioactive wastes processing, as well. These methods are in a relatively early stage of development, although they are expected to find applications in nuclear industry in the future.

Membrane distillation

Membrane distillation (MD) avoids disadvantages of pressure-driven membrane methods as concentration polarization and fouling phenomena resulted in the need of regular cleaning operations and production of secondary wastes. The process was proposed and developed at the INCT for liquid radioactive waste processing [21].

Membrane distillation is a separation method which employs porous lyophobic membrane, nonwettable by liquid. Because of lyophobicity of the polymer only vapour is transported through membrane pores. The condensation takes place on the other side of the membrane in air gap, cooling liquid or inert carrier gas. Usually, MD is employed to treat water solutions, therefore hydrophobic membranes, manufactured from

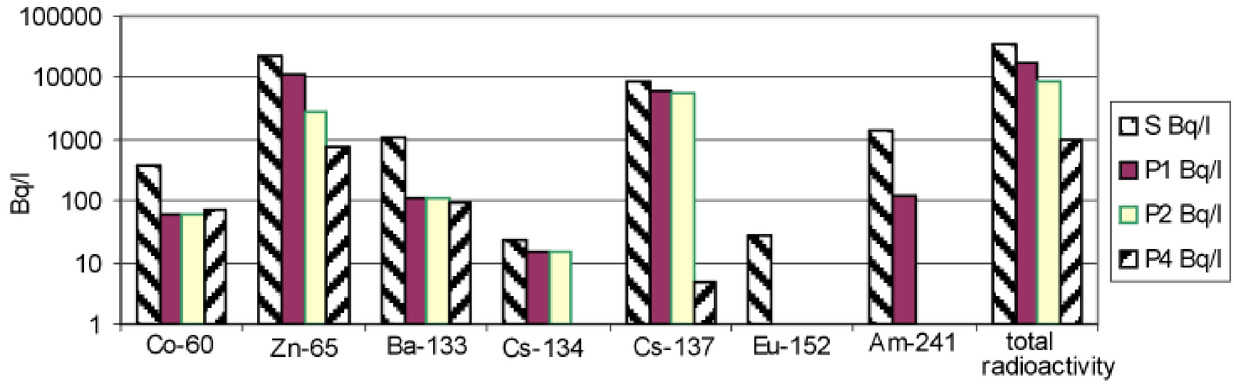

Fig. 3. Concentration of the radioactive components in feed solution (S) and permeate (P1, P2, P4) after the treatment in hybrid UF/complexation process.

such polymers like polypropylene (PP), polytetrafluoroethylene (PTFE) or poly(vinylidenefluoride) (PVDF) are used in the process. The driving force in the MD process is a gradient of partial pressures of the components of the solution in gaseous phase.

Case study: Membrane distillation for radioactive wastes concentration

The facility used at the INCT consists of industrial spiral-wound G-4.0-6-7 (SEP Gesellschaft für Technische Studien, Entwicklung, Plannung mbH) module, equipped with a PTFE hydrophobic membrane of 4 m^2 effective surface area. The process heat is supplied to the installation by a Navigator®, N40, 40 kW, (PEXEL) boiler combined with a heat CB51-20H (Alfa Laval, Poland) exchanger. Part of the heat lost in the process is recovered in the system of two heat exchangers (JAD X-6/50 and JAD 6/50).

The process of liquid radioactive waste concentration runs in the temperature range 35–80°C at the feed inlet, and 5–30°C at the distillate inlet, and with feed and distillate flow rates up to 1500 dm^3/h. Under these conditions, the permeate stream is 10–50 dm^3/h (60–300 dm^3/m^2day). During the plant operation, the activity of distillate remained stable on the level of natural background radioactivity and the concentration of radioactive compounds took place in the retentate (warm stream). As it was shown in the experiments, retention of radioactive ions in the retentate was almost complete (for most of radioisotopes the decontamination factor $\rightarrow \infty$). Most of radionuclides were not detected in the distillate; only trace amounts of Co-60 and Cs-137 were present [21].

The tests with radioactive solutions showed that some absorption of radioactive compounds took place in the membrane and entire unit as was presented in Fig. 4. Radioactive cobalt was added to the feed solution in two portions. The system was operated in continuous mode; the excess of distillate was returned back to the retentate tank. In such a way, the conductivity and radioactivity of both streams: retentate and distillate should remain on the stable level. However, after some hours a decrease of retentate radioactivity was observed, because of the sorption of radionuclides in the membrane. Despite of that, finally the saturation was achieved, the membrane has to be regularly washed to avoid the accumulation of radioactivity.

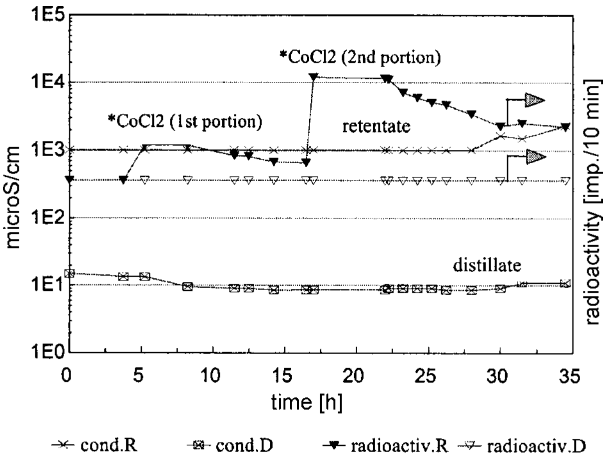

Fig. 4. Membrane distillation experiment with ^{60}Co solution.

Electric membrane processes

The processes driven by electrical potential use ion exchange membranes allowing selective transport of ions or other electrically charged molecules through the membrane. They have a number of advantages as minimization of secondary wastes, moderate process conditions, low capital and operational costs. The main processes in this group, tested for radioactive waste treatment are: electroosmosis, electrodialysis, membrane electrolysis.

There are descriptions of these processes used for radioactive waste processing in the literature [15, 16].

Liquid membranes

The processes applying liquid membranes are driven by concentration gradient. The membrane separates two phases (liquid or gaseous) from each other. Because of differences in the solubility and diffusivity in the liquid film of the membrane, the separation of solution components occurs. Membrane can be formed as a thick layer (BLM – bulk liquid membrane), immobilized in porous support (SLM – supported liquid membrane) and as emulsion droplets with the addition of surfactant (ELM – emulsion liquid membrane). In case of liquid membranes, the mass transport surface is big and this improves the separation. To enhance the selectivity, the carrier of high affinity to one of the separated components is introduced into the membrane. Such a process is known as facilitated transport or carrier mediated transport. Liquid membranes are applied in nuclear industry for the separation of actinides or other metals from radioactive waste [8, 17].

Recycling and reuse opportunities

Membrane processes allow not only purification of waste streams, but also play a meaningful role in many recovery and reuse schemes in industry and environmental protection. The conservation of natural resources, rational use of raw materials and water are very important aims of clean technologies. These objectives are not so evident in case of processing of radioactive streams. In that case the most important goals are purification of the effluents and reduction of the volume of radioactive species. However, in perspective of increased water scarcity and exhaustion of natural resources, the recovery of some valuable materials used within the fuel cycle or water recycling and reuse will become the point of interest. Membrane processes are very useful techniques for such purposes. The main recycling and reuse opportunities for nuclear field are shown in Table 1.

Water recovery, reuse or recycling

One of the most often recycled and reused substances is water that can be recovered by many membrane

Table 1. Recycling and reuse opportunities

Recovery and recycling possibilities	Possible membrane processes applied
Water recovery, reuse or recycling	Reverse osmosis, nanofiltration, ultrafiltration, microfiltration, membrane distillation, pervaporation
Boric acid recovery for recycling	Nanofiltration, ultrafiltration
Recycling of detergents and complexing agents	Nanofiltration, ultrafiltration
Recycling of rare and valuable metals	Ultrafiltration with sorption, liquid membranes, electrodialysis
Separation and partitioning of actinides	Ultrafiltration, enhanced ultrafiltration, liquid membranes
Tritium recovery	Gas separation, membrane distillation

processes. Reuse of water decreases the environmental discharge, saves water resources and conserves the supply of freshwater. In the future, the wastewater recovery and reuse will be no longer an option, but an absolute necessity. Extreme operation conditions of many plants around the world will be zero liquid discharge strategy. Water recycling is motivated entirely by economics; the cost of purification to provide the water of quality commensurate with that of the freshwater supply is perceived as being less than that of the freshwater and waste discharge.

The best-developed method of water reclamation is reverse osmosis. The other pressure-driven processes like NF, UF or MF are used in combination with other techniques of treatment. Good alternative for RO seems MD that produces very clean water that can by recycled in a technological process or reused for some other purposes.

Case studies:

Example 1: Reverse osmosis for water recycling

In a reverse osmosis plant at Świerk, described above, water recovered after the second purification pass is of radiochemical purity. Pilot plant experiments showed that usually specific radioactivity of permeate after the second stage is below 10 Bq/l and the total salinity is equal to several mg/l. This water can be discharged to the municipal sewage, however it is more reasonable to use it in some other process or recycle to the installation as washing water. One of the problems of pressure-driven membrane processes is a membrane fouling that is serious because of flux decline and membrane blockage. There are many ways to avoid the fouling phenomenon including the feed-water pretreatment and promoting the turbulence in apparatus. However, in spite of all these efforts there is a necessity of regular cleaning of the membrane and installation. The produced permeate can be used for that purpose.

Example 2: Membrane distillation for water reclamation and reuse [21]

Membrane distillation can be an alternative method of water reclamation. The process produces very pure permeate of parameters comparable with distilled water. This water can be used as clean water for boilers or heating installations or as water washing the installation as well. In Fig. 5, the results of purification of water of different initial salinity in the range of 0.5–16.5 g/l, are presented. The process was performed with MD

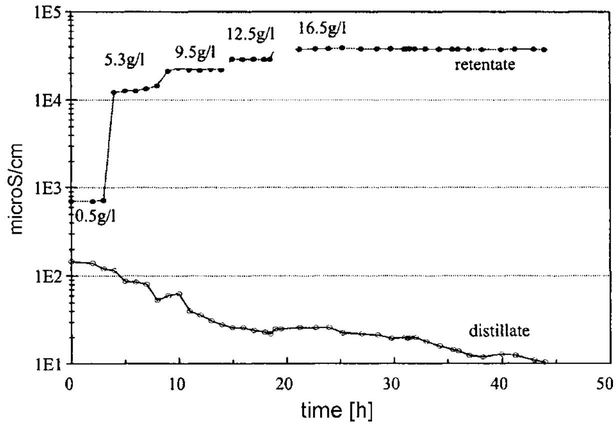

Fig. 5. Purification of water of different KCl content by MD.

installation equipped with the spiral wound G-4.0-6-7 module described above. During the experiment, the distillate was returned to the feed water tank. Potassium chloride did not pass through the membrane, it remained in retentate stream and purification of water took place on the other side of the membrane: specific conductivity of distillate decreased with time. All non-volatile impurities in wastewater are concentrated in a warm stream; on the cold side of the membrane clean water is produced.

Boric acid recovery and recycling

By use of nanofiltration or ultrafiltration it is possible to separate and recover boric acid from reactor cooler. Radioactive fission and corrosion products retain in retentate, and boric acid passes through the membrane and is collected in permeate [2, 12].

Recycling of detergents

There is a possibility of removal of detergents or complexing agents for recycling with use of such processes like nanofiltration or ultrafiltration [3, 14]. There are detergents in the waste from laundries washing contaminated clothes. Because of foaming it is difficult to clean the wastes in evaporator. The use of membrane processes avoids this disadvantage and allows separating detergents for recycling. The detergents are passing through the membrane and are collected in permeate; the other particles and radionuclides are retained in retentate.

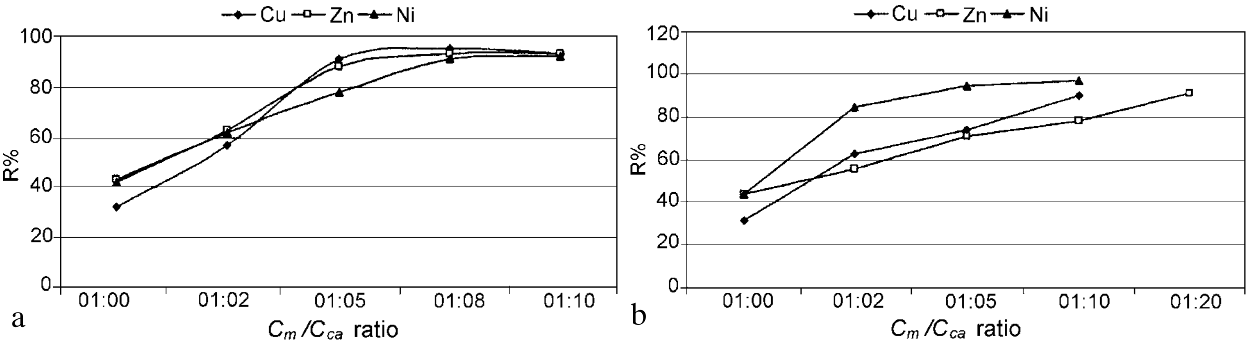

Fig. 6. Removal of metals in process of ultrafiltration enhanced by complexation with soluble chelation polymers: a – polyacryliacid as a complexing agent; b – polyethylenimine as a complexing agent.

Recycling of metals

Some metals like lithium, zinc or zirconium are important for nuclear technology. It is reasonable to recover them from the process streams. In some instances valuable by-products (vanadium, molybdenum, copper, nickel, arsenic, gold, rare earths and yttrium) can be produced from the process liquors obtained by leaching of uranium ores.

The processes of ultrafiltration combined with sorption or complexation can be selective for lanthanides(III) and actinides(III) [5], as well as the process of electrodialysis. The metal ions are bound by macromolecules of the complexing agents or by inorganic sorbents. In the next stage, the sorbent or complexing agent is regenerated and the metals are discharged.

Liquid membranes using different organic compounds that are applied in extraction (crown ethers, organophosphorous compounds, tertiary amines) show selectivity for some specific metals and can be used for effective recovery of those metals from process liquors.

<u>Case study</u>: Removal of metals in UF/complexation hybrid process

Process of ultrafiltration enhanced by polymer chelation for removal of metals from water solution was carried out. Polyacrylic acid and polyethtylenimine were used as complexing agents. The polymer was added in concentration corresponding to metal to polymer ratio C_m/C_{ca} in the range 1:2–1:20. After achieving the equilibrium (several hours), the solution was treated with Membralox® ceramic membranes. In Fig. 6, the results of removal of copper, zinc and nickel ions with a membrane of pore size 50 nm are shown. The retention of metal ions depended strongly on the C_m/C_{ca} ratio. Optimal C_m/C_{ca} ratio depended both on the metal extracted from the solution and the polymer type. The intensity of removal depends on the pH of, solution as well. By selection of process conditions and polymer type, one can remove different metals from various wastewater streams.

Partitioning and separation of actinides

There is a need to separate the long-lived actinides from the waste or spent nuclear fuel in a small volume before the disposal or for transmutation. There are also recovery techniques used for production of uranium from phosphoric acid or from other process streams.

Actinides are separated mainly in the process of extraction developed for this purpose. Liquid membranes can be selective for actinides; they have also many advantages over bulk extractants. They use less of extracting compounds, which are sometimes expensive. The other advantages of liquid membranes over solvent extraction derive from more favourable kinetics and smaller equipment used.

Ultrafiltration combined with sorption or complexation can separate and partition the actinides, too. First of all, the process is used as a stage in radioactive waste processing before disposal, however some valuable actinides can be recovered [5]. Recent developments have greatly extended membrane types and applications, including inorganic membranes and supported liquid membranes.

Tritium recovery

Tritium removal from liquid and gaseous wastes created by nuclear reactors or fuel reprocessing plants is a very important problem of radioactive waste treatment. The research on separation of hydrogen isotopes by permeation methods concerns the issues related to nuclear reactor safety and removal of tritium from process streams – from nuclear reactor waters or from exhaust gases, and tritium created during fuel reprocessing. Much of space is devoted to the studies concerning future thermonuclear fuel cycle safety [4, 18].

<u>Case study</u>: Separation of tritium from water solutions by membrane distillation

Vapour enhanced membrane distillation was proposed for the removal of trace amounts of tritium from water solution. The set-up, like in Fig. 7, was equipped with a porous FGLP (Millipore) membrane from polytetra-fluoroethylene, pore size 0.1 μm. As a feed solution, distilled water with an admixture of HTO, specific activity 148 Bq/dm^3, was used. The process was conducted in the temperature range (20–82) ± 0.5°C, the pressure in a vapour chamber being (0–84) ± 2 torr. The separation factors $\alpha_{H_2O/HTO}$ obtained in the process were in the range 1.03–1.22. They were higher than the separation factors for the distillation of water, which correspond to the relative volatility factors of two isotopomers of water: H_2O and HTO (Fig. 8).

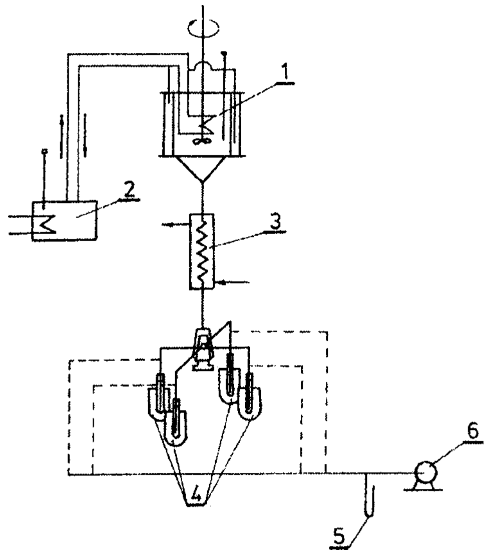

Fig. 7. A set-up for vapour enhanced membrane distillation experiments. 1 – Permeation chamber; 2 – thermostatted vessel with feed solution; 3 – cooler; 4 – samplers; 5 – manometer; 6 – rotation pump.

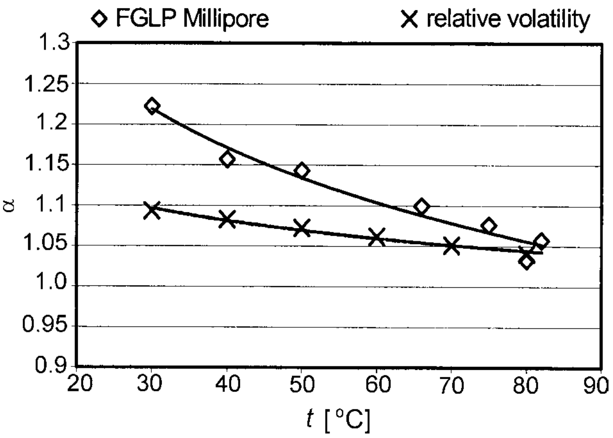

Fig. 8. Separation factors in membrane process with relation to relative volatility factors.

New energy sources, energy recovery systems

One of the strategic goals of clean technologies is the rational use of energy. This term includes effective energy recovery systems, as well as the use of cheap energy sources, especially renewable sources and waste heat.

Nuclear power plants produce great amounts of waste heat that can be used to drive some technological processes as evaporation, membrane distillation or pervaporation. Some of these processes can be applied for radioactive waste treatment directly in the place where they are created. This option is beneficial, because eliminates the costs of transport to the place of processing and allows water recovering and minimizing the environmental discharges. The waste heat can be used for the production of fresh water from seawater by application of technology known as a "nuclear desalination" [13]. Nuclear desalination that uses the heat supplied by nuclear reactor applies common distillation techniques for production of fresh water, as well as membrane techniques like reverse osmosis, electrodialysis or membrane distillation. While membrane distillation is driven by heat produced by nuclear system, reverse osmosis uses electric energy. However, heating up the feed water delivered to RO system increases markedly the productivity of the plant. Apart from the waste heat, membrane distillation can be driven with the heat supplied by other cheap energy sources like solar energy, geothermal or tidal energy. This seems to be economic technology wherever is used.

Despite of relatively low energy consumption in membrane processes much of efforts are being done to continuous improvement of the economy of these methods. In high pressure RO installations it is possible to recover some part of the energy used for pumping and establishing high pressure by application of work recovery systems, booster pumps, Pelton turbines, etc., [1, 11]. The energy of pressurised retentate is utilized to supplement part of the energy to run the installation. The aim of rational use of energy and raw materials is realized also by economic and flexible hybrid systems. These systems allow more rational use of energy and better adjustment of the product parameters according to the actual needs.

Case study: Nuclear desalination of seawater by hybrid MD/RO method [22]

In Fig. 9, an example of membrane desalination system is seen that employs MD integrated with RO and nuclear reactor supplying the energy for both installations. MD unit is driven with the heat from cooling circuit of the reactor, RO with electric power produced by turbine moved by high-pressure steam from the generator. The feed water delivered to RO modules is heated up by waste heat (MD retentate), that results in higher productivity of RO plant. Additionally, the RO installation is equipped with work recovery system that allows recovering a part of the energy used for generation of high pressures in this unit. The hybrid solution allows flexible adjusting the parameters of the product water and rational use of energy. It combines the advantages of two processes: high desalination performance of membrane distillation and low energy consumption of reverse osmosis. The hybrid system reduces total operational costs. Both plants have common seawater intake facilities and post-treatment facilities. Blending the water produced by two

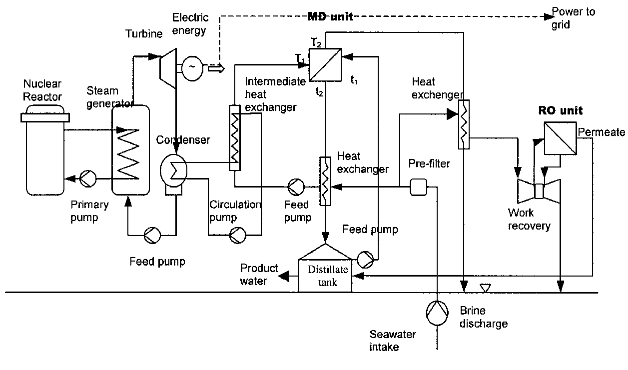

Fig. 9. Hybrid nuclear desalination system employing MD and RO with work recovery.

installations is possible. RO plant can be designed to produce water with higher level of total dissolved salts and thus lowers water production costs. It uses the electricity from the power plant and can operate during periods of reduced power demand (off-peak), thus allows optimizing the overall efficiency of the operation. Membranes have found application in the field of new energy sources: for the production of hydrogen for fuel cells and separation of hydrogen isotopes for fusion reactors [13, 18], as well as for methane enrichment in biogas [10].

Conclusions

Membrane processes may contribute to solving different problems of natural environment conservation. They save raw materials, minimize energy consumption and allow realizing various recovery strategies. Membranes can be easily combined in economic hybrid systems that permit free adjustment of product parameters and energy use. By their versatility and multiple functions, membrane methods can fulfil various aims and expectations of strategy of clean technologies.

All membrane methods are very efficient, however high separation ability of each membrane process is limited to some specific range of separated particles. Reverse osmosis is capable to retain all dissolved species including monovalent ions, but it applies high pressures that are unnecessary when thermally driven process, e.g. membrane distillation, which has similar separation capabilities, is used. In industrial-scale systems, the application of membrane distillation seems reasonable when cheap thermal energy sources are available. The plants that produce the waste heat like power stations are reasonable places for implementation of such processes. The other pressure-driven membrane methods like ultrafiltration, nanofiltration and microfiltration are efficient for separation of bigger particles. Nanofiltration has good efficiency in the separation of monovalent ions from organic molecules or from bivalent ions, in that way the process creates various recovery opportunities. Ultrafiltration and microfiltration are efficient at the separation of colloids and suspended matters with high recovery factors. The fluxes obtained in those processes are much more higher than in reverse osmosis; they can be used for dewatering of big volumes of sludge and sediments after precipitation. The advantages of membrane methods come from a big variety of different processes operated in different ranges of process parameters and separated particle sizes, as well as from their flexibility and facility of integration with other separation methods.

References

1. Andrews WT, Laker DS (2001) A twelve-year history of large scale application of work-exchanger energy recovery technology. Desalination 138:201–206
2. Astruc C, Baumgartner C, Bonneau S, Viricel L (1999) Filtration in nuclear power plants. In: Proc of the Int Conf Euromembrane'99, Leuven, Belgium 2:402
3. Barnier R, Caminade S, Loudenot L, Maurel M, Courtois F (1989) Ultrafiltration treatment of laundry liquid wastes from a nuclear research centre. In: Proc of the Int Conf on Waste Management, Kyoto, Japan
4. Bridesell SA, Willms RS (1998) Tritium recovery from tritiated water with a two-stage palladium membrane reactor. Fusion Eng Des 39/40:1041–1048
5. Chitry F, Pellet-Rostaing S, Gozzi C, Lemaire M (2000) Lanthanides(III)/actinides(III) separation by nanofiltration-complexation in aqueous medium. In: Proc of the Int Conf on Nuclear Waste: From research to industrial maturity, Montpellier, France, pp 868–871
6. Chmielewski AG, Harasimowicz M, Tymiński B, Zakrzewska-Trznadel G (2001) Concentration of low- and medium-level radioactive wastes with 3-stage reverse osmosis pilot plant. Separ Sci Technol 36;5/6:1117–1129
7. Cumming IW, Williams GH, Gutman RG, Davison CG (1992) Development of combined precipitation and ultrafiltration process and its application to the treatment of low active wastes. IAEA-SM-303-21P. IAEA, Vienna
8. Dozol JF (1991) Application of CMPO extractant (supported liquid membrane) for alpha decontamination of Marcoule reprocessing concentrate. Report EUR-13390-EN, Commission of the European Communities. Elsevier Applied Science, pp 95–105
9. European Commission, Directorate-General Environment (2003) LIFE FOCUS/Industrial pollution, European solutions: clean technologies, LIFE and the directive on integrated pollution prevention and control (IPPC Directive), Luxembourg: Office for Official Publications of the European Communities
10. Harasimowicz M, Zakrzewska-Trznadel G, Chmielewski AG (2004) Application of membrane methods in the processes of biogas conditioning. In: Monographs of the Committee of Environmental Engineering of Polish Academy of Sciences. Vol. 22, pp 429–433
11. Harris C (1999) Energy recovery for membrane desalination. Desalination 125:173–180
12. IAEA (1996) Processing of nuclear power plant waste streams containing boric acid. IAEA-TECDOC-911. Vienna
13. IAEA (2000) Introduction of nuclear desalination. A guidebook. Technical Reports Series No. 400. Vienna
14. Kichik VA, Maslova MN, Svitzov AA, Culeshov NF (1987) Method for complex treatment of laundry liquid radioactive wastes by ultrafiltration. At Energ 63;2:130–134 (in Russian)
15. Lounis A, Gavach C (1997) Treatment of uranium leach solutions by electrodialysis for anion impurities removal. Hydrometallurgy 44:83–96
16. Sugimoto S (1987) Removal of radioactive ions from nuclear waste solutions by electrodialysis. J Nucl Sci Technol 15:753–759
17. Teramoto M, Fu SS, Takatani K *et al.* (2000) Treatment of simulated low level radioactive wastewater by supported liquid membranes: uphill transport of Ce(III) using CMPO as carrier. Sep Purif Technol 18:57–69
18. Tosti, S, Violante V, Basile A *et al.* (2000) Catalytic membrane reactors for tritium recovery from tritiated water in the ITER fuel cycle. Fusion Eng Des 49/50:953–958
19. Zakrzewska-Trznadel G (2003) Radioactive solutions treatment by hybrid complexation – UF/NF process. J Membrane Sci 225:25–39
20. Zakrzewska-Trznadel G, Harasimowicz M (2002) Removal of radionuclides by membrane permeation combined with complexation. Desalination 144:207–212
21. Zakrzewska-Trznadel G, Harasimowicz M, Chmielewski AG (1999) Concentration of radioactive components in

liquid low-level radioactive waste by membrane distillation. J Membrane Sci 163:257–264
22. Zakrzewska-Trznadel G, Khayet M, Mengual J (2005) The concept of application of membrane distillation for nuclear desalination. In: Proc of the Int Conf ICOM2005, Seoul, Korea. Final program and abstracts, p 97