

THE USE OF ULTRAFILTRATION AND REVERSE OSMOSIS IN THE
DESALINATION OF LOW MINERALIZED GEOTHERMAL WATERS

BARBARA TOMASZEWSKA

Mineral and Energy Economy Research Institute
Polish Academy of Sciences
Wybickiego 7, 31-261 Kraków
Corresponding author's e-mail: b.tomaszewska@meeri.pl

Keywords: Geothermal water, reverse osmosis, desalination, water balance.

Abstract: Compared to other European countries, Poland has scarce drinking water resources and exhibits significant variation in annual runoff. On the other hand, the geothermal water resources present in sedimentary/structural basins, mostly in the Polish Lowlands and the Podhale geothermal system, not only provide a valuable source of renewable energy, which is utilized, although only to a limited extent, but can also be used for many other purposes. The paper presents the results of studies related to the desalination of low dissolved mineral content geothermal waters from the Bańska IG-1 well using a dual hybrid system based on ultrafiltration and reverse osmosis. The desalination of geothermal waters may be considered a possible solution leading to the decentralization of drinking water supply. In many cases, using cooled waters for drinking purposes may be considered an alternative method of disposing of them, in particular for open drain arrangements, i.e. where cooled water is dumped into surface waters.

INTRODUCTION

Drinking water shortages in many regions of the world have contributed to the development of water treatment technologies. Simple treatment methods such as filtration, coagulation, sedimentation and high performance membrane and thermal desalination technologies have been gradually modified and upgraded since the mid-20th century. Hybrid systems that combine the advantages of multiple desalination technologies are also increasingly coming into focus. They have become a widely used method of producing water for drinking and household purposes.

Compared to other European countries, Poland has scarce drinking water resources and exhibits significant variation in annual runoff. Shortages are reflected by the absence of groundwater reservoirs in some regions and the significant quantitative and qualitative anthropogenic pressure to which major aquifers are often subject [28, 45]. On the other hand, the geothermal water resources present in sedimentary/structural basins, mostly in the Polish Lowlands and the Podhale geothermal system (Podhale Basin), not only provide a valuable source of renewable energy (which is utilized although only to a limited extent) but can also be used for many other purposes [14]. The thermal water is either extracted using submersible pumps or it flows by itself when the deposits are under artesian pressure. Extraction is carried out using:

- a closed system of production and injection wells: cooled geothermal water is injected back into the reservoir through the well after partial heat recovery in heat exchangers or heat pumps;
- an open system of production wells: after partial heat recovery cooled water is not injected back into the reservoir but is transferred to a surface reservoir or utilized in another way, e.g. as potable water (if it meets the relevant quality standards) or to fill swimming pools.

In the second case, an open drain system operation (without injecting cooled water into the formation) has significantly improved the economic performance of the enterprise.

In Poland, geothermal water resources are associated with the presence of large regional underground reservoirs. The use of cooled, lightly mineralized geothermal water for drinking purposes, particularly for open drain installations (without injecting cooled water into the formation) will contribute to the comprehensive utilization of geothermal fluid and the decentralization of drinking water production. It would also be a more effective use of the water released, including an improvement in the water balance and water management.

Membrane-based water desalination processes and hybrid technologies that combine membranes processes are widely used to produce drinking water in many regions of the world. They are also considered a technologically and economically viable alternative for desalinating water (mainly seawater), often with the use of renewable (solar, wind, geothermal, photovoltaic) energy.

The paper presents possible use of dual hybrid system based on ultrafiltration and reverse osmosis methods to desalinating of cooled geothermal water, which may be used in order to produce drinking water, what is shown in experiences of geothermal water treatment from Bańska IG-1 well.

MEMBRANE TECHNOLOGIES

The total capacity of desalination plants around the globe is $59.9 \cdot 10^6 \text{ m}^3 \text{ d}^{-1}$. There was an increase of $6.6 \cdot 10^6 \text{ m}^3 \text{ d}^{-1}$ in the year 2008, and it is the largest amount of desalination capacity brought online in the single year [31]. In 2001, the total worldwide desalination plant capacity amounted to $32.4 \cdot 10^6 \text{ m}^3 \text{ d}^{-1}$, which was almost three times higher than 10 years earlier [6, 14]. About 80% of the world's desalination capacity is provided by two technologies: multi-stage flash evaporation (MSF), and reverse osmosis (RO) [31]. There is an increasing trend to replace distillation by membrane methods, mainly by reverse osmosis (RO). The operation costs of RO were reduced over the years due to development of low-cost efficient membranes, usage of pressure recovery devices and also renewable energy. Seawater RO cost has gone down to about $0.53 \text{ \$ m}^{-3}$ in Ashkelon at the Mediterranean Sea [31, 36]. Currently, owing to the reduction in cost that was achieved in the last 20 years, it is a generally accepted method.

A desalting process essentially separates saline water into two streams: permeate, with a low concentration of dissolved salts (the fresh water stream) and the other containing the remaining dissolved salts (the concentrate/retentate).

Membrane processes, which are driven by the pressure difference on both sides of the membrane (microfiltration, ultrafiltration, nanofiltration and reverse osmosis) [5, 21,

33], are mostly used for concentrating and/or purifying diluted aqueous solutions. Under the pressure applied, the solvent and low molecular weight solutes pass through the membrane, while other molecules with higher molecular weight, colloids and fine suspensions cannot cross it. Depending on whether microfiltration, ultrafiltration, nanofiltration or reverse osmosis is involved, particles with increasingly smaller molecular weights are blocked. The area of application determines the size of the particles that the membrane retains. Technologies based on the solution-diffusion mechanism range from reverse osmosis with the most compact membranes that are only permeable to water, through nanofiltration, with membranes that make it possible to separate ions with different valences and ultrafiltration with membranes that retain fine suspensions, colloids, bacteria and viruses, to microfiltration membranes with the largest pores that are able to retain macrosuspensions [8].

Within the present technological and theoretical framework, membrane technologies are utilized in the following areas [5, 7, 8, 9]:

- reverse osmosis (RO) used to retain ions and most low molecular weight organic compounds; it is primarily employed in the desalination of water and wastewater as well as to remove metal ions, inorganic anions and other low molecular weight organic compounds;
- a nanofiltration membrane (NF) used to retain colloids, many low and medium molecular weight organic compounds and divalent ions; it can be used to soften water and to remove organic and inorganic micropollutants from water and wastewater;
- ultrafiltration (UF) and microfiltration (MF) membranes serve as a barrier to dispersed substances, including colloids and microorganisms. The membranes can be used to remove these from water and wastewater, as well as within the framework of membrane-based and thermal desalination and demineralization processes. Moreover, they are utilized in integrated/hybrid arrangements in processes such as coagulation – UF/MF, powdered activated carbon adsorption – UF/MF, biological filtration – UF/MF, oxygenation (ozonation and others) –UF/MF and in membrane bioreactors.

REVERSE OSMOSIS

A typical reverse osmosis water desalination plant consists of a raw water pretreatment system, a membrane desalination system including a high pressure pump and a final treatment system whose purpose is adaptation to the requirements for drinking water. Figure 1 presents the most important components of an RO desalination plant [1, 8, 14].

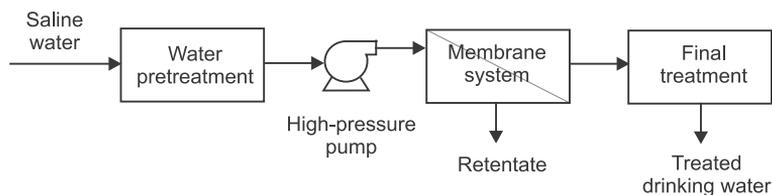


Figure 1. RO water desalination plant — simplified diagram [after 5,14]

The RO process is affected by a particular problem associated with its performance, namely fouling, i.e. the permanent, often irreversible, change in membrane permeability caused by many different factors. Fouling is the deposition of substances (suspended mat-

ter, colloids, soluble macromolecular compounds, salts) on the membrane surface and/or in the pores, which reduces membrane permeability. It is caused by organic and inorganic substances as well as suspended matter [5, 8, 20, 26, 32]. Another operational problem is membrane scaling caused by such substances as CaCO_3 , CaSO_4 and BaSO_4 ; the intensity of this phenomenon depends on the permeate/raw water volume ratio. At a desalinated water recovery ratio of 50%, this phenomenon can be effectively reduced by adding divalent ion complexing agents (so-called antiscalants) to water.

Around 80% of membranes currently used for RO purposes are composite membranes [2]. Two trends can be observed in the studies conducted during the last years: the introduction of low pressure RO membranes used for desalination and the use of high pressure membranes that offer higher efficiency compared to conventional ones [30, 44]. As concerns modifications of RO desalination membranes, work is underway on the development of membranes that would operate at higher temperatures of up to 45°C (which results in increased plant capacity without the need to increase the membrane surface), improving the service life of membranes, reducing the scope of water pretreatment and minimizing fouling and scaling [3]. The development of innovative technologies, nanocomposite, nanotube, and biomimetic membranes is also promising [39].

The characteristics of a membrane-based arrangement, and, in general, of a membrane in operation, are described by two parameters: 1) permeability (permeate flux), which defines the membrane's performance; and 2) selectivity, which defines the membrane's ability to separate solution components. Permeate flux refers to the volume, mass or number of moles of the substance that passes a unit area of the membrane per unit time. For separation techniques, membrane selectivity is defined as the ratio of the permeate composition to that of the input mixture (feed). On the other hand, membrane permeability (L) depends on the solubility of a substance passing through the membrane and its diffusion coefficient. For reverse osmosis membranes, this ranges from 10^{-6} to 10^{-8} $\text{m}^3\text{m}^{-3}\text{d}^{-1}\text{Pa}^{-1}$. The mass flux of the dissolved substance (J_s) passing through the membrane depends solely on the differential in the concentrations of this substance on both sides of the membrane, which is described by the following formula [8]:

$$J_s = Ls \cdot (C_s - C_p)$$

where:

Ls – membrane permeability with respect to the dissolved substance;

C_s – the concentration of the dissolved substance in the feed solution;

C_p – the concentration of the dissolved substance in the permeate.

The membrane's separation properties are described by the value of the retention coefficient (R) for the key compound:

$$R = \frac{C_n - C_p}{C_n} = 1 - \frac{C_p}{C_n}$$

where:

C_p – compound concentration in the permeate;

C_n – compound concentration in the feed.

LOW MINERALIZED GEOTHERMAL WATER RESERVOIRS IN POLAND

The geothermal water reservoirs that are currently being exploited in Poland exhibit varied physical properties (temperature, pH, conductivity) and chemical composition. Both

fresh waters with low dissolved mineral content (about 0.5 to 10 g L^{-1} in Mszczonów, Podhale — Zakopane-Antałówka, Zakopane-Szymoszkowa, Bukowina Tatrzańska, Cieplice Zdrój, Łądek Zdrój, Bańska Nizna, Uniejów) and brines with mineralization exceeding 100 g L^{-1} (Pyrzyce, Stargard Szczeciński, Ustroń) are exploited in the country [11, 13, 14, 15, 25]. Geothermal energy resources are associated with groundwater present at depths of up to 3000 m within certain regional geological units: the Polish Lowlands, the Carpathians, the Carpathian Foredeep and the Sudetes (Fig. 2).

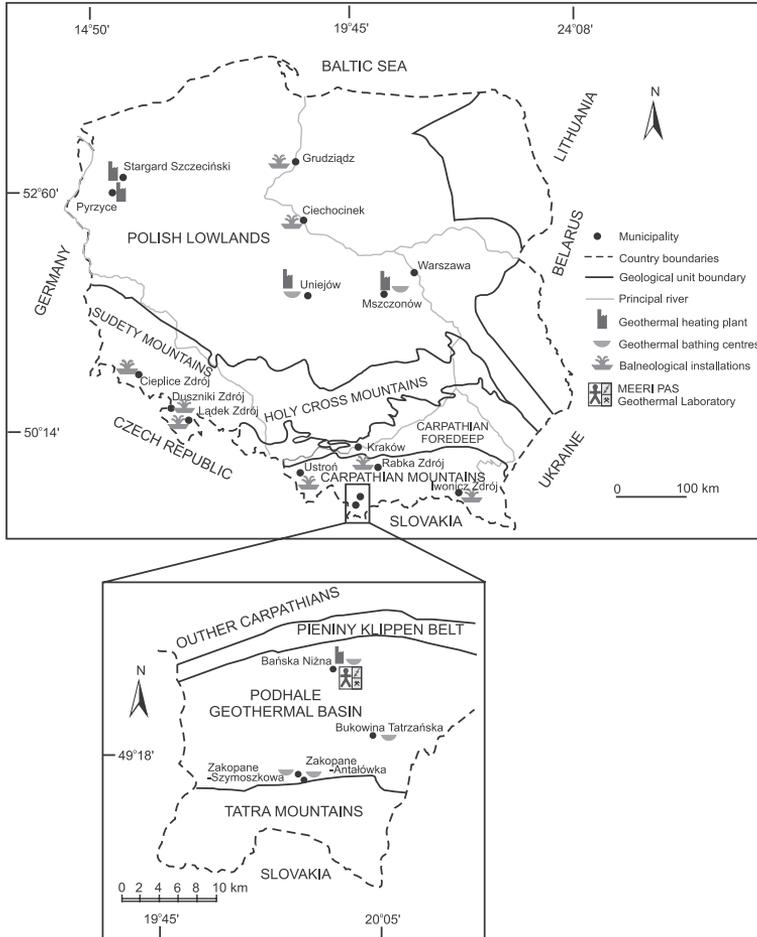


Figure 2. Location of geothermal facilities in Poland against the background of geothermal units [after 14]

Low mineralized water are exploited especially from the Lower Cretaceous reservoir and Podhale Basin. The Lower Cretaceous reservoir has an area of $115\,521 \text{ km}^2$, i.e. 40% of the area of Poland. It forms a complex of discontinuous, interspersed sandy, sandy-marly and sandy-mudstone layers with thicknesses ranging from a few to 300 m . The TDS values do not exceed 40 g L^{-3} , at the temperature varying from 20 to about 80°C . The top part of the Lower Cretaceous formation occurs at various altitudes from about $+250 \text{ m asl}$ to below -2500 m asl . Within the dominant part of the reservoir, water tem-

perature ranges from 20 to 40°C, only in some areas temperatures rise to over 50°C being related to the deepest structural depressions [22, 23, 38, 40, 41]. In Mszczonów in Central Poland (Fig. 2), weakly mineralised water (below 0.5 g/dm³) with a temperature of 42°C is being extracted from a Lower Cretaceous horizon composed of sandstones interspersed with mudstone and claystone via the Mszczonów IG-1 well. This is high quality Cl-HCO₃-Na-Ca water. After cooling using an absorption pump and treatment (filtration and disinfection), the water is used for consumption purposes in the municipal water supply system. A second geothermal aquifer in Uniejów, also situated in Central Poland (Fig. 2), is hosted in Cretaceous sandstones at a depth of about 2000 m. Wellhead temperature is about 60°C and TDS is 5 g L⁻¹. The water is exploited in a one dublet system. The geothermal fluid is exploited for heating and also is used for recreational purposes.

The most favorable hydrogeological conditions for the presence of geothermal waters in Poland exist within the Podhale geothermal system (Podhale Basin) (Fig. 2). This geothermal reservoir consists of several aquifers present within Triassic limestone and dolomite, Jurassic sandstone and carbonate rocks and within Eocene carbonate formations [17, 25, 29, 37]. The aquifers lie directly beneath the insulating cover of Podhale flysch (Upper Eocene–Oligocene). The thickness of the reservoir rocks ranges from 100 to 700 m. Maximum artesian flow rates from wells range from 90 to 550 m³ h⁻¹, and water temperatures range from 20 to 90°C depending on the depth from -660 m to -3500 m. The mineralization of geothermal waters ranges from less than 200 mg L⁻¹ within the Tatra massif to 3000 mg L⁻¹ in the northern part of the reservoir. The Tatra area provides an infiltration supply to underground aquifers, so the resources found there are of a renewable nature [12, 13, 14, 16, 17, 25, 41, 42]. The geothermal waters sourced in the area are mainly used for heating (PEC Geotermia Podhalańska S.A.) and recreational purposes (Zakopane-Antałówka, Zakopane-Szymoszkowa, Bukowina Tatrzańska, Szaflary).

PILOT GEOTHERMAL WATER DESALINATION TESTS

The first desalination project concerned water from the Bańska IG-1 well (the aquifer from which these geothermal waters are extracted lies at a depth of 2565 m), located at the Geothermal Laboratory of the Mineral and Energy Economy Research Institute of the Polish Academy of Sciences in Kraków (PAS MEERI) (Fig. 2).

The aforementioned location was chosen for pilot studies owing to the relatively low mineralization of the geothermal waters from the Bańska IG-1 well (2.9 g L⁻¹), high admissible volume of extracted groundwater (120 m³ h⁻¹) and the deficit of fresh water in the well area (the villages of Bańska Niżna and Szaflary) [42]. The capacity of local fresh water intakes covers only 20% of local demand (around 500 houses). The Bańska IG-1 well forms part of the geothermal direct heating circuit operated by the major operator of the Podhale geothermal system — the PEC Geotermia Podhalańska SA company. The geothermal heating system supplies energy for district heating and heating household water to single- and multi-family houses as well as public buildings. Small volumes of the water are also used at the Termy Podhalańskie geothermal spa which was launched in 2008. After being cooled using heat exchangers, usually to around 50°C, some geothermal water (approximately 50%) is injected back into the formation via the injection well, and some is discharged into the nearby river (it is allowed by legislation) [14, 42]. Efficient use of the thermal energy accumulated in the water extracted and the comprehensive

utilization of cooled water, for drinking water among other purposes, would make it possible to optimize geothermal water management and improve the balance of fresh water in the area examined.

METHODS AND APPARATUS

Taking into account water salinity (2.9 g L^{-1}) and the increased content of silica (62.5 mg L^{-1}), hydrogen sulfide and other sulfides (0.085 mg L^{-1}), boron (9.95 mg L^{-1}), barium (0.142 mg L^{-1}), strontium (7.19 mg L^{-1}), ammonium ions (1.3 mg L^{-1}), fluorides (1.3 mg L^{-1}), bromides (1.75 mg L^{-1}) and sulfates (872 mg L^{-1}), a double hybrid setup was selected that combined ultrafiltration and reverse osmosis [14]. The water desalination facility includes the following components (Fig. 3):

- a water pretreatment facility: mechanical filter, iron removal stage and ultrafiltration module (UF membranes with a module diameter of 8" and a pore size of $0.03 \mu\text{m}$),
- a two-stage reverse osmosis setup with NaOH dosing before stage two (DOW FILMTEC BW30HR-440i osmosis membranes, designed for brackish water with increased silica, boron, ammonium and nitrate content),
- final treatment to achieve drinking water parameters (mineralization, sterilization).

The desalination plant is fed with unmodified geothermal waters, with a temperature not exceeding 35°C , at a steady flow rate of $4\text{--}5 \text{ m}^3 \text{ h}^{-1}$ with a natural content of dissolved gases (mostly carbon dioxide, hydrogen sulfide and nitrogen). Owing to its gas content, the water fed into the plant pulsed and problems were encountered at the iron removal stage. Therefore, it was necessary to fit an air bleeder system at the feeding stage and remove gas from the catalytic bed iron removal tank.

The installation was fitted with two ultrafiltration modules including UFC M5 (X-Flow) hydrophilic capillary polyethersulfone membranes with a total filtration surface area of 80 m^2 .

In the pilot facility, DOW FILMTEC BW30HR-440i RO membranes were used for geothermal water desalination; these are polyamide thin-film composite membranes with a maximum operating temperature of 45°C , a maximum operating pressure of 41 bar, admissible pH range 2 to 11 and a maximum feed Silt Density Index (SDI) of 5. These membranes may be used in drinking water applications. According to the data quoted by the membrane manufacturer, a minimum salt rejection is 99.4%, stabilised rejection for silica (SiO_2) is 99.9%, while for boron it is 83% at a pressure of 15.5 bar, water temperature of 25°C and a feed pH of 8. The reverse osmosis stage consists of the following modules (pressure pipes): RO-1 – two modules, RO-2 – one module. Each module includes one osmosis membrane.

For a neutral or slightly acidic feed reaction membrane selectivity does not ensure high boron retention. Boron is a non-metallic element with atomic number 5, an atomic weight of 10.81, and an oxidation number of 3. In chemical terms, boron – just like silicon and carbon – tends to form covalent bonds [10, 18, 27]. But unlike these elements it has one valence electron less compared to the number of valence orbitals. This "shortage of electrons" has a fundamental impact on the course of chemical processes involving boron. Boron atoms are small and move easily; their migration patterns change significantly depending on water reaction [4, 19, 43]. The modelling of the thermodynamic state of geothermal waters from the Bańska IG-1 well has shown that for a neutral water reac-

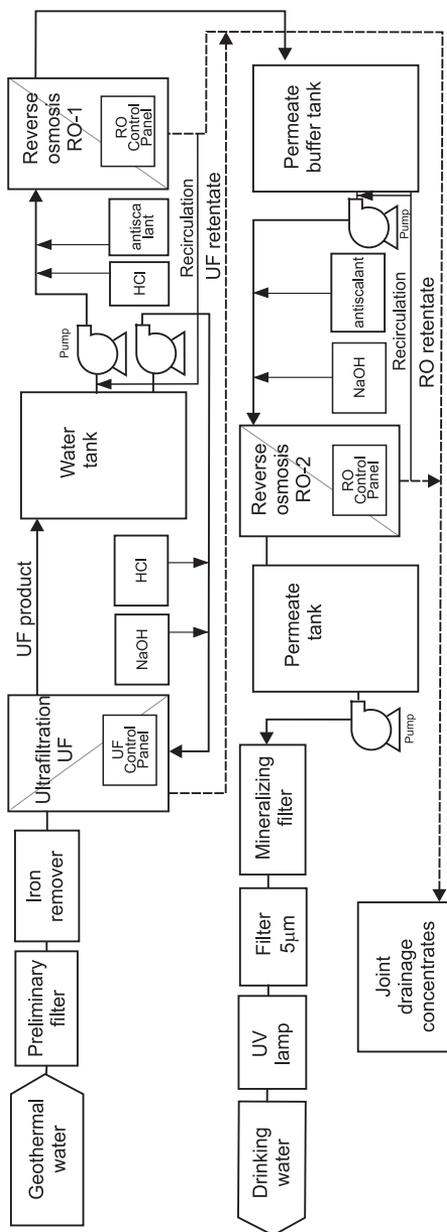


Figure 3. Technological diagram of the geothermal water desalination facility

tion (raw water from the Bańska IG-1 well), 98% of boron is present as undissociated boric acid (H_3BO_3^0). The remaining 2% is found as H_2BO_3^- metaboric ions and polyboron fluorides; $\text{BF}(\text{OH})_3^-$, $\text{BF}_2(\text{OH})_2^-$, BF_3OH^- and BF_4^- . After the reaction had been adjusted to slightly acidic (a pH of 5–6), boric acid became the dominant form of boron in the water (99.98%). Conversely, for a pH of more than 10, the main form of boron migration (95.53%) was the H_2BO_3^- metaboric anion. In view of the above relationships, a test of membrane separation properties was conducted at a constant pressure of 11 bar and variable feed reaction ranging from a pH of 3 to 11 (Fig. 4) in order to optimise the boron removal process. Favourable retention ratios of 96 and 97% were obtained for pH values of 10 and 11, respectively.

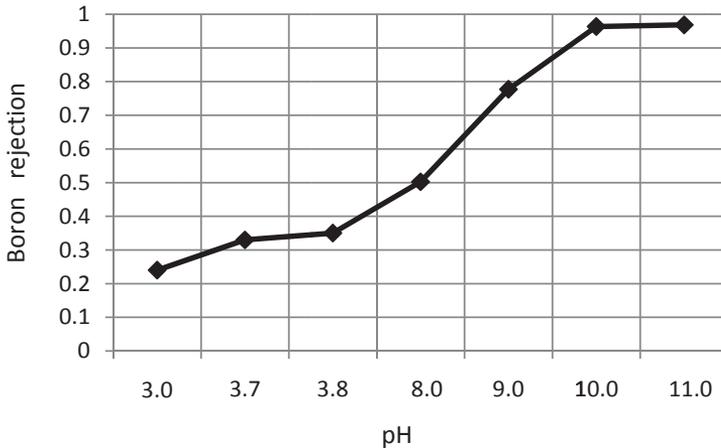


Figure. 4. Boron retention ratios as a function of feed pH

One of the main operational problems when using RO technology is membrane fouling and scaling. The chemical equilibrium of the solution was calculated (Fig. 5) using PHREEQCI programs [34].

Figure 5a shows differences in the SI (saturation index) values calculated for carbonate, sulphur and silica minerals in raw water from the Bańska IG-1 well. It was shown as a result of calculations that in a temperature of 30°C and neutral pH there are good conditions for the precipitation of aragonite, barite, calcite, chalcedony, dolomite and quartz on the RO membranes.

The tendency to form calcium carbonate from waters was also calculated using the Langelier Saturation Index (LSI) and the Ryznar Stability Index (RSI) [35]. The LSI and the RSI are equilibrium models derived from the theoretical concept of saturation and provide an indication of the degree of saturation of water with CaCO_3 . The calculation showed:

- LSI = 0.029 and pHs = 7.4, which means that the water is supersaturated with respect to calcium carbonate (CaCO_3) and scale formation may occur. Slight formation of scale and corrosive;
- RSI = 7.3 and pHs = 7.4, water is aggressive and corrosion can occur.

It is important to point out that the accuracy of the RSI and LSI is much greater as a predictor of scaling than of corrosion. This results from the fact that both methods are

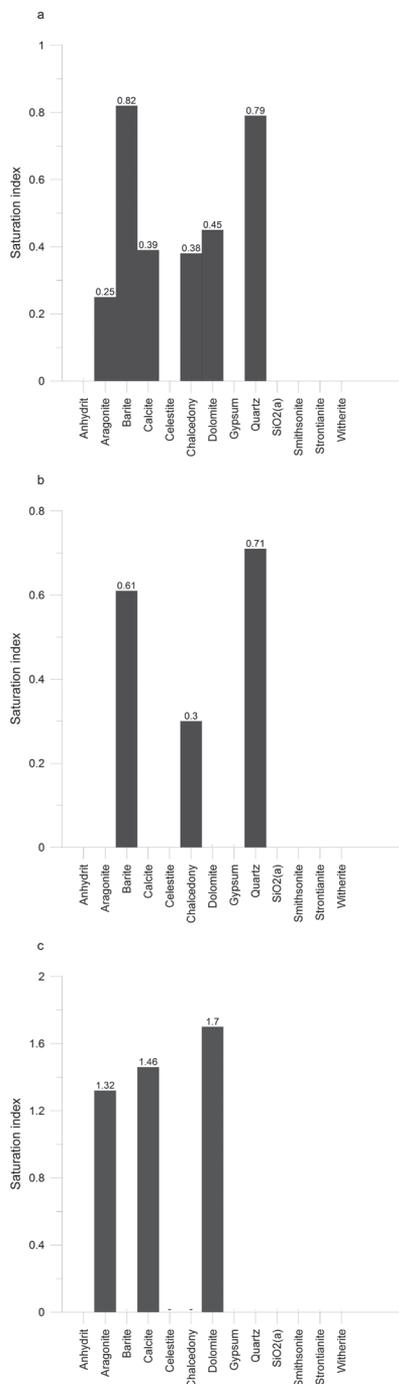


Fig. 5. Precipitation propensity depending on water type: a) raw water from Bańska IG-1 well; b) water after UF, before RO-1 following pH adjustment towards slightly acidic (pH 5–6); c) water after RO-1, before RO-2 following pH adjustment towards alkaline (pH 10)

based upon the saturation of calcium carbonate. The assumption implicit in the calculations is that if the calcium carbonate content exceeds the level that can be maintained in solution, scale will occur [35].

Therefore Hydrex 4109, an antiscalant (a substance complexing divalent ions), was added before the water was fed to RO membranes in order to prevent their fouling and scaling. The theoretical antiscalant dosage was calculated on the basis of the chemical composition of the water, but after just a few hours of continuous operation, RO performance dropped and membranes had to be regenerated. A positive aspect was the ease with which membranes could be restored to their initial state by chemical etching (chemical bathing). This indicates that it is mainly calcium carbonates, and not sulphates, that are deposited on osmosis membranes. Antiscalant dosage was modified and additional doses of diluted hydrochloric acid were used. Currently, pH is modified to 5–6 before RO-1.

The fact that a slightly acidic reaction of the water fed to the first stage of the reverse osmosis facility is maintained reduces the possibility of sediment precipitation on the surface of the membrane. The modelling of the thermodynamic state of pre-treated water (following iron removal and UF and after a pH adjustment to 5–6) demonstrated that a propensity towards silicate mineral and low-solubility barite precipitation was still present, but there was no propensity towards carbonate mineral precipitation (Fig. 5 b). A pH adjustment before the second osmosis stage makes it possible for aragonite, calcite and dolomite to precipitate again, but this process occurs on a limited scale since the water fed to the RO-2 stage is already desalinated to a large extent (Fig. 5 c, Table 1, 2).

Table 1. Chemical composition of geothermal water and water at individual desalination stages.

Parameter	Geothermal water	After UF	After RO-1	After RO-2	Desalin. water	Maximum allowable concentration
Arsenic mg L ⁻¹	0.00075	0.0028	0.00025	0.00012	0.00010	0.010
Nitrates mg L ⁻¹	<0.50	<0.50	<0.50	<0.50	<0.50	50
Boron mg L ⁻¹	9.46	9.45	6.07	0.16	0.01	1.0
Chromium mg L ⁻¹	0.0019	0.0019	0.0016	0.0016	0.0016	0.050
Cadmium mg L ⁻¹	0.00018	0.00003	0.00001	0.00001	0.00001	0.005
Copper mg L ⁻¹	0.0032	0.0016	0.00067	0.00055	0.00088	2.0
Nickel mg L ⁻¹	0.0029	0.0011	0.00018	0.00002	0.00002	0.020
Lead mg L ⁻¹	0.001	0.001	0.00096	0.00052	0.00046	0.025
Mercury mg L ⁻¹	0.00014	0.00014	0.00013	0.0001	0.0001	0.001
Selenium mg L ⁻¹	0.001	0.001	0.001	0.001	0.001	0.010
Chlorides mg L ⁻¹	527.0	520.0	13.4	13.4	13.4	250
Aluminum mg L ⁻¹	0.015	0.005	0.005	0.005	0.005	0.200
Manganese mg L ⁻¹	0.041	0.040	0.002	<0.001	<0.001	0.050
pH	7.2	6.87	5.38	9.49	6.97	6.5–9.5
Conductivity $\mu\text{S cm}^{-1}$	3550	3230	195	104	195	2500
Sulfates mg L ⁻¹	938.2	915.18	8.10	6.40	6.40	250
Sodium mg L ⁻¹	545.1	543.9	21.0	19	19	200
Iron mg L ⁻¹	4.0	0.013	0.009	0.008	0.004	0.200
Magnesium mg L ⁻¹	42.71	41.7	0.24	<0.10	<0.10	30–125
Silver mg L ⁻¹	0.0066	0.001	0.00058	0.00013	0.00013	0.010
Hardness mg CaCO ₃ L ⁻¹	679.3	674.3	3.8	0	93.5	60–500

Table 2. Retention coefficients (%) for key compounds: macro-elements and micro-elements after RO-1 and RO-2.

Parameter	After RO-1	After RO-2
Arsenic	0.95	0.96
Boron	0.48	0.96
Chromium	0.73	0.73
Copper	0.75	0.79
Nickel	0.88	0.93
Lead	0.55	0.69
Chlorides	0.84	0.97
Aluminum	0.67	0.67
Manganese	0.99	0.99
TDS	0.93	0.95
Sulfates	0.99	0.99
Sodium	0.92	0.95
Iron	0.98	0.99
Calcium	0.95	0.95
Magnesium	0.99	0.99
Potassium	0.92	0.94
Lithium	0.95	0.99
Barium	1.00	1.00
Strontium	0.99	0.99
Silica	0.94	0.98
Zinc	0.97	0.97

RESULTS DISCUSSION

The reduction in iron concentration from ca. 4 mg L⁻¹ to 0.013 mg L⁻¹ (Table 1) was obtained by using an iron removal system. Water pressurised to around 3–5 bar passes an MTM catalyst bed layer. Oxidised iron hydroxides, which precipitate in the form of flakes that settle easily, are retained on the surface of the catalyst bed. The bed is regularly rinsed to remove the precipitated oxidised iron compounds and regenerated at fixed intervals using a chemical oxidant (potassium permanganate – KMnO₄). After major pollutants have been filtered out and iron has been removed, the water is fed to the ultrafiltration (UF) module. Following UF, water electrolytic conductivity and hardness decrease by around 10% and simultaneously a significant (30% to 60%) drop in aluminium content is observed. No reduction in silica concentration was found during the water pre-treatment process; this results from the fact that silica is not present in colloidal form in thermal waters (silicic acid H₄SiO₄ accounts for 99% of silica content).

RO modules are fed with water at a temperature of ca. 30°C and pressure of 11-15 bar. RO-1 membrane permeability with a 78% desalinated water recovery rate amounts to ca. 5.25 10⁻⁶ m³ m⁻²s⁻¹; for RO-2, it is 7.9 10⁻⁶ m³ m⁻²s⁻¹ with a desalinated water recovery rate of ca. 75%. A relatively high retention rate was obtained following the first RO stage – 93% with respect to TDS and 94% with respect to SiO₂ (Table 2).

The preliminary research results indicate that, apart from its boron content, the permeate obtained following the first RO stage of geothermal water desalination meets the general requirements for drinking water (Table 1). According to their technical specifications, the DOW FILMTEC BW30HR-440i osmosis membranes used exhibit a boron retention coefficient of 83% at a pressure of 15 bar. This means that the maximum boron content in raw water for a single-stage reverse osmosis system (however, only for an alkaline feed reaction) should not exceed 1.7–1.8 mg L⁻¹. Therefore, since the boron concentration in water had to be reduced from almost 10 mg L⁻¹ to a maximum of 1 mg L⁻¹, a two-stage desalination system was required. Following the addition of antiscalant and an increase in pH to 10, the permeate output from the first RO stage was fed to a second RO stage.

The application of a two-stage desalination system significantly reduces the drinking water recovery ratio. On the other hand, a high divalent ion content makes it impossible to adjust the water reaction towards alkaline before the first RO stage, since this would cause the precipitation of sediments and the fouling of the osmosis membranes.

Taking into account significant water hardness and the propensity towards sediment precipitation, nanofiltration (NF) may provide an alternative to the water pre-treatment arrangement adopted that uses ultrafiltration. Possible benefits might include:

- the removal of divalent ions during the pre-treatment process;
- a decrease in the mineral content of the solutions fed to the RO facility;
- the operation of the RO facility without the need to use any additional chemicals, mainly hydrochloric acid.

CONCLUSIONS

The desalination of low dissolved mineral content geothermal waters using membrane-based technologies may be considered a possible solution leading to the decentralization of drinking water supply. The research conducted at the Geothermal Laboratory of the PAS MEERI using a dual hybrid system based on ultrafiltration and reverse osmosis has demonstrated that high-quality water may be obtained even after the first RO stage. System extension, i.e. the addition of a second RO stage together with pH adjustment, is required where high water boron content is present.

Geothermal energy is being used for heating purposes to an ever greater extent. In many cases, using cooled waters for drinking purposes may be considered an alternative method of disposing of them, in particular for open drain arrangements, i.e. where cooled water is dumped into surface waters. However, the utilization or disposal of the concentrate in a fashion that is safe for the environment is an important part of the arrangement. Ideas and study results related to the possibility of using the concentrate produced in geothermal water desalination processes for balneological or industrial purposes will be the subject of subsequent publications.

REFERENCES

- [1] Aim R.B., M. Vladan: *The role of membrane techniques in cleaner production*, Industry and Environment, **12**, 15–18 (1989).
- [2] Alley W. M.: *Desalination of Ground Water: Earth Science Perspectives*, U.S. Geological Survey, October (2003).

- [3] Baker R.: *Membrane technology in the Chemical Industry. Future directions*, [in:] *Membrane Technology in the Chemical Industry* (eds: S. P. Nunes, K.-V. Peinemann), Wiley-Vch, Weinheim, 268–295 (2001).
- [4] Blahusiak M., M. Schlosser: *Simulation of the adsorption-microfiltration processes for boron removal from RO permeate*, *Desalination*, **241**, 156–166 (2009).
- [5] Bodzek M., J. Bohdziewicz, K. Konieczny: *Techniki membranowe w ochronie środowiska*, Wydawnictwo Politechniki Śląskiej, Gliwice, Poland (1997).
- [6] Bodzek M., K. Konieczny, M. Dudziak: *Możliwości wykorzystania technik membranowych w procesach uzdatniania wody do picia* [in:] *Membrany i techniki membranowe — Od pomysłu do przemysłu* (ed.: M. Szwast), Polymem Ltd.sp. z o.o., Warszawa, 5–49 (2009).
- [7] Bodzek M., K. Konieczny: *Membrane processes in water treatment — State of art*, *Inżynieria i Ochrona Środowiska* **9**, 129–159 (2006).
- [8] Bodzek M., K. Konieczny: *Wykorzystanie procesów membranowych w uzdatnianiu wody*. Oficyna Wydawnicza Projprzem-EKO, Bydgoszcz, Poland (2005).
- [9] Bodzek M., K. Konieczny: *Skojarzone systemy membranowe w uzdatnianiu wody — stan wiedzy*, [in:] *Materiały VII Międzynarodowej Konferencji: „Zaopatrzenie w wodę, jakość i ochrona wód”*, Zakopane, tom I, 43–61 (2006).
- [10] Budavari S. (ed.): *The Merck index*, 11th ed. Rahway, NJ, Merck and Co., Inc. (1989).
- [11] Bujakowski W., A. Barbacki, B. Czerwińska, L. Pająk, M. Pussak, M. Stefaniuk, Z. Trzeźniowski: *Integrated seismic and magnetotelluric exploration of the Skierniewice, Poland, geothermal test site*, *Geothermics*, **39**, 78–93 (2010).
- [12] Bujakowski W., A. Barbacki, L. Pająk: *Atlas of geothermal water reservoirs in Malopolska*, PAS MEERI Publishers, Krakow, Poland, (2006).
- [13] Bujakowski W., A. Barbacki: *Potential for geothermal development in Southern Poland*, *Geothermics*, **33**, 383–395 (2004).
- [14] Bujakowski W., B. Tomaszewska, M. Bodzek: *Geothermal water treatment — preliminary experiences from Poland with a global overview of membrane and hybrid desalination technologies*, [in:] *Renewable energy for decentralized drinking water production* (eds.: J. Bundschuh, J. Hoinkis) (2011) – submitted.
- [15] Bujakowski W., B. Tomaszewska: *Program prac zmierzających do oceny możliwości uzdatniania wód termalnych*, Technika Poszukiwań Geologicznych Geotermia, Zrównoważony Rozwój, Kraków, Poland, 1/2007, 3–8 (2007).
- [16] Bujakowski W.: *The use of geothermal waters in Poland (state in 2009)*, *Przegląd Geologiczny*, **58**, 580–588 (2010).
- [17] Chowaniec J.: *Wody podziemne niecki podhalańskiej*, [in:] *Współczesne Problemy Hydrogeologii Gdańsk*, Poland, XI/1, 45–53 (2003).
- [18] Cotton PA, L. Wilkinson: *Advanced inorganic chemistry*, 5th ed. New York, NY, John Wiley & Sons, 162–165 (1988).
- [19] Dydo P., M. Turek, J. Ciba, J. Trojanowska, J. Kluczka: *Boron removal from landfill leachate by means of nanofiltration and reverse osmosis*, *Desalination*, **185**, 131–137 (2005).
- [20] Fritzmann C., J. Löwenberg, T. Wintgens, T. Melin: *State-of-the-art of reverse osmosis desalination*, *Desalination*, **216**, 1–76 (2007).
- [21] Gawroński R.: *Membranowe procesy rozdzielania mieszanin*, *Instalator*, 7/8, 12–17 (2004).
- [22] Górecki W. (ed): *Atlas of geothermal resources of Mesozoic formations in the Polish Lowlands*, GÓLDRUK, Poland (2006).
- [23] Górecki W.: *Geothermal waters in the Polish Lowlands*, *Przegląd Geologiczny*, **58**, 574–579 (2010).
- [24] Greenlee L. F., D. F. Lawler, B. D. Freeman, B. Marrot, P. Moulin: *Reverse osmosis desalination: water sources, technology and today's challenges*, *Science Direct*, **43**, 2317–2348 (2009).
- [25] Kępińska B.: *Thermal and hydrothermal conditions of the Podhale geothermal system (Poland)*, PAS MEERI Publishers, Krakow, Poland (2006).
- [26] Kołtuniewicz A.: *Wydajność ciśnieniowych procesów membranowych w świetle teorii odnawiania powierzchni*, Oficyna Wydawnicza Politechniki Wrocławskiej, Wrocław, Poland (1996).
- [27] Kot F. S.: *Boron sources, speciation and its potential impact on health*, *Rev Environ Biotechnol*, **8**, 3–28 (2009).
- [28] Kyzioł-Komosińska J., C. Rosik-Dulewska, M. Pająk, M. Jarzyna: *Removal of direct dyes from wastewater by sorption onto smectite-clay*, *Archives of Environmental Protection*, **36** (3), 3–14 (2010).
- [29] Małecka D.: *Hydrogeologia Podhala*, *Prace Hydrogeologiczne*. Instytut Geologiczny, Wyd. Geologiczne, Warszawa, Poland 14 (1981).
- [30] Matsuura T.: *Progress in membrane science and technology for seawater desalination — a review*, *De-*

- salination, **134**, 47–54 (2001).
- [31] Mezher T., H. Fath, Z. Abbas, A. Khaled: *Techno-economic assessment and environmental impacts of desalination technologies*, *Desalination*, **266**, 263–723 (2011).
- [32] Mulder M.: *Basic Principles of Membrane Technology*. Kluwer Academic Publishers, Dordrecht-Boston-London (1991).
- [33] Nareńska A. (ed.): *Membrany i membranowe techniki rozdzielania*, Wydawnictwo Uniwersytetu Mikołaja Kopernika, Toruń, Poland (1997).
- [34] Parkhurst D. L., C. A. J. Appelo: User's guide to PHREEQCI (version 2) – a computer program for speciation, batch-reaction, one-dimension transport and inverse geochemical calculations: U.S Geological Survey Water-Resources Investigation Report 97–4259 (1999).
- [35] Rafferty K.: *Scaling in geothermal heat pump systems*, U.S. Department of Energy Idaho Operations Office 785 DOE Place Idaho Falls, ID 83401 (1999).
- [36] Sauvet-Goichon B.: *Ashkelon desalination plant – A successful challenge*, *Desalination*, **203**, 75–81 (2007).
- [37] Sokołowski S.: *Geologia paleogenu i mezozoicznego podłoża południowego skrzydła niecki podhalańskiej w profilu głębokiego wiercenia w Zakopanem*, Biuletyn IG, Warszawa, Poland 265 (1973).
- [38] Strzetelski W.: *Geologiczna charakterystyka zbiorników wód geotermalnych na Niżu Polskim*, [in:] Atlas wód geotermalnych Niżu Polskiego (ed: W. Górecki), Archiwum Katedry Surowców Energetycznych AGH, Kraków, Poland, 49–55 (1990).
- [39] Subramani A., M. Badruzzaman, J. Oppenheimer, J. G. Jacangelo: *Energy minimization strategies and renewable energy utilization for desalination: A review*, *Water research* **45**, 1907–1920 (2011).
- [40] Szczepański A.: *Warunki hydrotermalne dolnojurajskiego i dolnokredowego zbiornika geotermalnego–zbiornik dolno kredowy*, [in:] Atlas wód geotermalnych Niżu Polskiego (ed: W. Górecki), Archiwum Katedry Surowców Energetycznych AGH, Kraków, Poland 316–322 (1990).
- [41] Szczepański A.: *Zbiornik dolnokredowy–warunki hydrotermalne*, Atlas zasobów energii geotermalnej na Niżu Polskim (ed: W. Górecki) Wyd. AGH, Kraków, Poland 13 (1995).
- [42] Tomaszewska B.: *Treatment of geothermal water from Banska IG-1 well to produce drinking water as one of directions of its wide use*, Technika Poszukiwań Geologicznych Geotermia, Zrównoważony Rozwój, Kraków, 2/2009, 21–28 (2009).
- [43] Turek M., P. Dydo, J. Trojanowska, A. Campen: *Adsorption/co-precipitation-reverse osmosis system for boron removal*, *Desalination*, **205**, 192–199 (2007).
- [44] Van der Bruggen B., Vandecasteele C.: *Distillation vs. membrane filtration: Overview of process evolutions in seawater desalination*, *Desalination*, **143**, 207–218 (2002).
- [45] Wiatkowski M.: *Impact of the Small Water Reservoir Psurów on the Quality and Flows of the Prosna River*, *Archives of Environmental Protection*, **36** (3), 84–96 (2010).

Received: April 11, 2011; accepted: July 5, 2011.

WYKORZYSTANIE ULTRAFILTRACJI I ODWRÓCONEJ OSMOZY W ODSALANIU NISKOMINERALIZOWANYCH WÓD TERMALNYCH

Polska, w porównaniu z innymi krajami europejskimi, posiada niewielkie zasoby wód pitnych i duże wahania rocznego odpływu. Z drugiej strony zasoby wód geotermalnych, wstępujące w basenach sedymentacyjno-strukturalnych głównie Niżu Polskiego i podhalańskiego systemu geotermalnego (niecki podhalańskiej), mogą stanowić cenne źródło nie tylko energii odnawialnej, wykorzystywane wciąż jeszcze w ograniczonym zakresie, ale potencjał o wielokierunkowym zastosowaniu. W pracy przedstawiono wyniki badań związanych z odsalaniem nisko zmineralizowanych wód geotermalnych eksploatowanych otworem Bańska IG-1 przy zastosowaniu dwuhybrydowego systemu opartego na ultrafiltracji i odwróconej osmozie. Odsalanie wód geotermalnych może być rozważane jako jedna z alternatyw w decentralizacji dostaw wody pitnej. Zagospodarowanie schłodzonych wód do celów pitnych może w wielu przypadkach być rozpatrywane jako sposób ich utylizacji, w szczególności w systemach pracujących w układzie otwartym, tj. w przypadku zrzutu wód schłodzonych do cieków powierzchniowych.