Geothermal water treatment. Membrane selection for the RO process

Barbara Tomaszewska\textsuperscript{a,b,*}, Michał Bodzek\textsuperscript{c,d}, Mariola Rajca\textsuperscript{a}, Magdalena Tyszer\textsuperscript{a}

\textsuperscript{a}AGH University of Science and Technology, Faculty of Geology, Geophysics and Environmental Protection, Department of Fossil Fuels, Mickiewicza 30 Av., 30-059 Kraków, Poland, email: barbara.tomaszewska@agh.edu.pl
\textsuperscript{b}Mineral and Energy Economy Research Institute, Polish Academy of Sciences, Wybickiego 7, 31-261 Kraków, Poland, email: b.tomaszewska@meeri.pl
\textsuperscript{c}Institute of Environmental Engineering, Polish Academy of Sciences, M. Curie-Skłodowskiej 34, 41-819 Zabrze, Poland
\textsuperscript{d}Silesian University of Technology, Institute of Water and Wastewater Engineering, Konarskiego 18, 44-100 Gliwice, Poland

Received 2 June 2016; Accepted 9 July 2016

ABSTRACT

Many factors determine the effectiveness of membrane processes used in the desalination of water. One of the most critical of these is the careful selection of membranes which have selective parameters and permeability suited to the needs of the user. The paper presents the results of studies related to the selection of membranes for the process of desalinating mineralised geothermal waters with an elevated silica content, sulphate ions, boron ions and high total hardness. Based on the preliminary theoretical models, four commercially available types of membranes were identified, which were then used for laboratory tests. Particular attention was paid in this work to the selectivity of removal of boron ions and also the effectiveness of the process in conditions of respectively 50\% and 75\% permeate recovery. Tests were carried out on geothermal water at a temperature 22°C. The results of the studies carried out showed that the best permeability parameters in relation to time taken were found with the BW30HR-440i membrane at a level of 50\% permeate recovery. An increase in permeate recovery to 75\% demonstrated signs of a drop in performance with time which may be caused by the precipitation of deposits on the membrane and the lowering of its permeability. Favourable selectivity ratios in relation to the key inorganic components of the mineral water were obtained with the selected membrane.

Keywords: Membrane selection; Geothermal water; Water treatment; Reverse osmosis

1. Introduction

Over the last century, global population has tripled while water demand per capita has doubled resulting in a six-fold increase in water abstraction. This suggests that not only has the overall number of water users increased, but the individual consumption rate has also increased due to high living standards [1]. Various water treatment and desalination technologies have been developed, are under development, to cope with the scarcity of clean water at a global scale [1–6].

The reuse of treated waste-water and the desalination of sea water or brackish water, including geothermal water, have emerged as reliable solutions to this serious problem [1,6–9]. The utilisation of membrane techniques in industrial-scale water desalination processes is associated with the very careful selection of technological systems. It must have a regard to the reliable operation of the system in an energetically sustainable way, with simultaneous optimisation in the recovery of the desired raw material, which is pure water. One of the most critical of these is the careful selection of membranes which have selective parameters and permeability suited to the needs of the user, in particular when steps are being
taken to desalinate geothermal waters. The composition of geothermal water is determined by the macro-elements in the reservoir rock and the subsurface environment to which it is exposed most of the time. The most frequently observed elements with high concentrations are Na⁺, K⁺, Ca²⁺, Mg²⁺, HCO₃⁻, CO₃²⁻, SO₄²⁻, and CO₂. Other micropollutants are heavy metals such as mercury, copper, lead, silver, iron, zinc, arsenic, manganese, chromium, beryllium, selenium, vanadium, cadmium, nickel, strontium, uranium, cobalt, gallium, and antimony. Some other elements including boron, silica, and elevated concentrations of radionuclides could be present in geothermal waters as well [1,8–11]. Boron, silica and the calcium hardness of water are serious problems if present in high concentrations. Numerous pieces of research devoted to the efficiency of removal of boron ions from water and wastewater during the process of reverse osmosis demonstrate that a high retention rate for boron, at a level exceeding 90%, is possible at a pH value of the water of at least 10 [10–20]. On the other hand, the presence of silica and increased water hardness may imply a tendency to scaling of the membrane during water desalination [21–25].

The paper presents the results of studies related to the selection of membranes for the process of desalination of mineralised geothermal waters. The studies carried out on a laboratory scale were focused on the selection of membranes which it was planned to use for further tests in an industrial pilot plant.

2. Method and process technology

2.1. Geothermal water

The water used for testing the selected membranes was obtained from the Bariska PGP-1 geothermal well and is characterised by elevated mineralisation (TDS 2.4 g L⁻¹), a high metasilic acid concentration (80 mg H₂SiO₃ L⁻¹), a high value of total hardness (650 mg CaCO₃ L⁻¹) and elevated concentrations of sulphates, boron and other macro and micronutrients. The raw water is of a hydrogeochemical type SO₄²⁻-Cl-Na-Ca based on the Szczukariewa-Pilkoskiego classification. The specific chemical and physical composition of the raw geothermal water were made at the beginning of technological tests. All tests were carried out using water at a temperature of 22°C.

2.2. Types of membranes

Four commercially available types of membrane were identified on the basis of preliminary theoretical models, and these membranes were then used for laboratory tests:

1. DOW FILMTEC™BW30FR-400 (Dow Water & Process Solutions Company);
2. DOW FILMTEC™BW30HR-440i (Dow Water & Process Solutions Company);
3. AG Membrane (GE Power Water & Process Technologies Company);
4. LEWABRANE®RO B400 HR (LANXESS Energizing Chemistry Company).

Each membrane is specially produced for use in water treatment systems based on the reverse osmosis process. All membranes are designed to purify the water and are characterised by a high retention coefficient of the undesirable components contained in water and fouling resistance in polluted waters.

The DOW FILMTEC™BW30FR-400 membrane used in the reverse osmosis test is designed to purify water with high biological or organic fouling potential in systems [26]. The membrane is characterised by a high rate of rejection of compounds, efficiency over a long life, exceptional fouling resistance and cleanliness.

The DOW FILMTEC™BW30HR-440i membrane used in the reverse osmosis test is described as a high-performing item with high productivity combining the largest active membrane area available in the industry today with a maximum rejection reverse osmosis (RO) membrane designed for brackish water [27]. It incorporates Dow’s innovative and proprietary BW30HR membrane sheet technology designed to deliver the highest quality RO permeate. This is combined with the cleanability of a 28 ml feed spacer, to minimise capital expenditure in high-purity industrial water applications, without increasing operating flux’ [27].

The LEWABRANE®RO B400 HR (PA00416HR(C12)) membrane, used in the reverse osmosis test, is designed for the industrial treatment of brackish and low salinity waters for primary demineralisation [28]. It is composite polyamide membrane, efficient and suitable for salt rejection (average 99.7%) [28].

The AG membrane (GE Power, Water & Process Technologies) used in the reverse osmosis test is characterised by high flux and high sodium chloride rejection [29]. It is efficient and appropriate for brackish waters where it can be used to reduce salinity and remove some chemical components.

2.3. Experimental procedure

Analyses were carried out to compare the efficiency of the reverse osmosis process in tests using different membranes. The assays were conducted by using the stirred cell device in “dead-end” mode, utilising a particular membrane, at a stable pressure of 15 bar. The raw water was placed in a stirred cell under the specified pressure. The active area of the membrane was 38 cm². During the study all the feed used was passed to the membrane and the concentrate was retained in the membrane. Reverse osmosis processes were carried out to obtain a 50% or 75% recovery of permeate with measurement being taken of the time required to receive each additional 5 ml of treated water. The membrane had a negative load surface in a wide range of pH values. Each of the membranes selected was conditioned by filtration of deionised water to check the efficiency of the membrane and obtain the value of the deionised water permeate flux. A schematic diagram of the reverse osmosis process system used in “dead-end” mode is shown in an article published earlier [30].
2.4. Analytical methods

The pH, electrical conductivity (EC) and temperature value of the water analysed was measured in the laboratory using the electrometric method immediately after obtaining permeate from the system. Inorganic components were determined in an accredited laboratory of the Department of Hydrogeology and Engineering Geology of the AGH University of Science and Technology in Kraków (PCA-tVB 1050) using the inductively coupled plasma mass spectrometry (ICP-MS) and (ICP-OS) methods. Water alkalinity and chloride ion content was specified by titration in accordance with accredited testing procedures.

3. Results and discussion

The results of the research carried out in relation to the selected physicochemical parameters for used geothermal water are shown in Tables 1 and 2.

3.1. The results of research with the use of the BW30FR-400 membrane

The value of the retention coefficient of the selected undesirable components in geothermal water following use of the BW30FR-400 membrane with 50% recovery are shown in Table 1 and those with 75% recovery are shown in Table 2. A high degree of retention of undesirable constituents was obtained in the tests with 50% recovery, with the exception of the boron ion (62%), which is the result of the low pH value (6.80) of the feed water [14]. For the survey conducted to obtain 75% recovery, the reduction of selected undesirable constituents increased in comparison with the 50%, except for the boron ion, in which retention decreased to 59%.

The process of desalinating geothermal water using a BW30FR-400 membrane with 50% recovery proceeded in a stable manner but with a slight decrease in permeate flux with time. The changes in permeate flux are shown in Fig. 1. In the research which was undertaken to obtain 75% recovery, the process also proceeded in a stable manner but with a significant decrease in permeate flux. Fig. 2 shows the changes in permeate flux with 75% recovery of feed water.

The tests on the treatment of geothermal water using the reverse osmosis process were subsequently carried out using other membranes.

3.2. The results of the research using the BW30HR-440i membrane

The value of measurements of the retention coefficient of the selected undesirable components in geothermal water after processing it with the use of a BW30HR-440i membrane with 50% recovery are shown in Table 1 and those with 75% recovery are shown in Table 2. The efficiency of retention is shown by the retention coefficient of the undesirable components in geothermal water after the process. The use of the BW30HR-440i membrane for 50% recovery is slightly better (about 10% higher) compared to the process with 50% recovery with the use of the BW30FR-400 membrane. The opposite trend was observed when comparing the BW30HR-440i and BW30FR-400 membranes.

Table 1
Results of the Bańska PGP-1 geothermal water using different reverse osmosis membranes, 50% permeate recovery (transmembrane pressure 15 bar, R-retention coefficient)

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Raw water (mg L⁻¹)</th>
<th>BW30FR-400 membrane</th>
<th>BW30HR-440i membrane</th>
<th>PA00416HR(C12) membrane</th>
<th>AG membrane</th>
</tr>
</thead>
<tbody>
<tr>
<td>aTH</td>
<td>655.40</td>
<td>3.2</td>
<td>99.5</td>
<td>0.3</td>
<td>99.95</td>
</tr>
<tr>
<td>Na⁺</td>
<td>488.681</td>
<td>10.733</td>
<td>97.80</td>
<td>8.638</td>
<td>98.23</td>
</tr>
<tr>
<td>K⁺</td>
<td>47.643</td>
<td>2.968</td>
<td>93.77</td>
<td>0.687</td>
<td>98.56</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>194.099</td>
<td>0.799</td>
<td>99.59</td>
<td>0.129</td>
<td>99.93</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>41.582</td>
<td>0.285</td>
<td>99.31</td>
<td>0.100</td>
<td>99.76</td>
</tr>
<tr>
<td>Sr²⁺</td>
<td>6.244</td>
<td>0.2</td>
<td>96.80</td>
<td>0.2</td>
<td>96.80</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>487.900</td>
<td>12.230</td>
<td>97.49</td>
<td>10.600</td>
<td>97.83</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>854.709</td>
<td>12.521</td>
<td>98.54</td>
<td>3.647</td>
<td>99.57</td>
</tr>
<tr>
<td>H₂SiO₃</td>
<td>79.43</td>
<td>1.76</td>
<td>97.78</td>
<td>1.30</td>
<td>98.36</td>
</tr>
<tr>
<td>Al³⁺</td>
<td>0.008</td>
<td>0.006</td>
<td>30.63</td>
<td>0.005</td>
<td>40.41</td>
</tr>
<tr>
<td>Fe²⁺</td>
<td>0.232</td>
<td>0.010</td>
<td>95.69</td>
<td>0.010</td>
<td>95.69</td>
</tr>
<tr>
<td>Ba³⁺</td>
<td>0.0436</td>
<td>0.0023</td>
<td>94.78</td>
<td>0.0005</td>
<td>98.85</td>
</tr>
<tr>
<td>B⁻³</td>
<td>9.76</td>
<td>3.71</td>
<td>61.99</td>
<td>3.66</td>
<td>62.50</td>
</tr>
<tr>
<td>EC [mS cm⁻¹]</td>
<td>3.35</td>
<td>0.088</td>
<td>97.37</td>
<td>0.051</td>
<td>98.48</td>
</tr>
<tr>
<td>pH</td>
<td>6.80</td>
<td>6.55</td>
<td>–</td>
<td>5.81</td>
<td>–</td>
</tr>
</tbody>
</table>

aTH, Total hardness [mg CaCO₃ L⁻¹]; EC, Electrical conductivity.
membranes for recovery at 75%. For the analysis which was carried out to obtain 75% recovery, the reduction of selected undesirable constituents decreased in comparison with the process with 50% recovery (for the processes with the use of the BW30HR-440i membrane). A beneficial reduction in total hardness of the solution was observed (for the process with 50% recovery): 99.95% for geothermal water after the process with the use of the BW30HR-440i membrane and 99.51% for the BW30FR-400 membrane. For the process with 50% recovery, the concentration of sulphate ions was decreased by 99.57% for the process with the use of the BW30HR-440i membrane and 98.54% for the BW30FR-400 membrane. The value of the retention coefficient for metasilicic acid increased from 97.78% for the process with the use of the BW30FR-400 membrane to 98.36% for the BW30HR-440i membrane. Boron reduction increased from 61.99% (for the BW30FR-400 membrane with 50% recovery) to 62.50% for the BW30HR-440i membrane with 50% recovery of geothermal water. The results of the test carried out to obtain 75% recovery with the use of the BW30HR-440i membrane demonstrated a lower retention coefficient for: total hardness 99.63%, boron ions 55.94%, sulphate ions 98.45% and metasilicic acid 97.73% than the BW30FR-400 membrane (respectively 99.92%, 59.12%, 99.40% and 98.40%).

The processes desalinating geothermal water with the use of the BW30HR-440i with 50% and 75% recovery proceeded with a considerable decrease in the permeate flux time, which indicated that a membrane scaling phenomenon had occurred (Fig. 1). The process with the use of the 30HR440i membrane and with 75% recovery of feed water

### Table 2

Results of Bańska PGP-1 geothermal water using different reverse osmosis membranes, 75% permeate recovery (transmembrane pressure 15 bar, R-retention coefficient)

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Raw water (mg L⁻¹)</th>
<th>BW30FR-400 membrane Permeate (mg L⁻¹) R (%)</th>
<th>BW30HR-440i membrane Permeate (mg L⁻¹) R (%)</th>
<th>PA00416HR(C12) membrane Permeate (mg L⁻¹) R (%)</th>
<th>AG membrane Permeate (mg L⁻¹) R (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TH</td>
<td>655.40 (0.5)</td>
<td>99.92</td>
<td>99.63</td>
<td>99.79</td>
<td>99.92</td>
</tr>
<tr>
<td>Na</td>
<td>488.681 (7.326)</td>
<td>98.50</td>
<td>97.72</td>
<td>97.25</td>
<td>97.66</td>
</tr>
<tr>
<td>K</td>
<td>47.643 (1.011)</td>
<td>97.88</td>
<td>96.80</td>
<td>97.84</td>
<td>98.40</td>
</tr>
<tr>
<td>Ca</td>
<td>194.099 (0.147)</td>
<td>99.92</td>
<td>99.69</td>
<td>99.80</td>
<td>99.91</td>
</tr>
<tr>
<td>Mg</td>
<td>41.582 (0.042)</td>
<td>99.90</td>
<td>99.50</td>
<td>99.72</td>
<td>99.91</td>
</tr>
<tr>
<td>Sr</td>
<td>6.244 (0.2)</td>
<td>96.80</td>
<td>96.80</td>
<td>96.80</td>
<td>96.80</td>
</tr>
<tr>
<td>Cl</td>
<td>487.900 (9.500)</td>
<td>98.05</td>
<td>97.03</td>
<td>97.32</td>
<td>97.66</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>854.709 (5.166)</td>
<td>98.40</td>
<td>98.45</td>
<td>98.79</td>
<td>98.60</td>
</tr>
<tr>
<td>H₂SiO₃</td>
<td>79.43 (1.27)</td>
<td>98.40</td>
<td>97.73</td>
<td>98.02</td>
<td>97.87</td>
</tr>
<tr>
<td>Al³⁺</td>
<td>0.008 (0.007)</td>
<td>18.62</td>
<td>40.41</td>
<td>40.41</td>
<td>37.40</td>
</tr>
<tr>
<td>Fe²⁺</td>
<td>0.232 (0.010)</td>
<td>95.69</td>
<td>95.69</td>
<td>95.69</td>
<td>93.70</td>
</tr>
<tr>
<td>Ba²⁺</td>
<td>0.0436 (0.0009)</td>
<td>97.94</td>
<td>97.33</td>
<td>98.85</td>
<td>98.85</td>
</tr>
<tr>
<td>B³⁺</td>
<td>9.76 (3.99)</td>
<td>95.12</td>
<td>55.94</td>
<td>55.84</td>
<td>46.41</td>
</tr>
<tr>
<td>EC [mS cm⁻¹]</td>
<td>3.35 (0.061)</td>
<td>98.18</td>
<td>97.28</td>
<td>97.67</td>
<td>98.09</td>
</tr>
<tr>
<td>pH</td>
<td>6.80 (6.65)</td>
<td>–</td>
<td>5.91</td>
<td>–</td>
<td>6.32</td>
</tr>
</tbody>
</table>

*TH, Total hardness [mg CaCO₃ L⁻¹]; bEC, Electrical conductivity.

![Fig. 1](image1.png)

Fig. 1. Changes of permeate flux during reverse osmosis of geothermal water using different membranes (50% recovery).

![Fig. 2](image2.png)

Fig. 2. Changes of permeate flux during reverse osmosis of geothermal water using different membranes (75% recovery).
proceeded with a significantly lower efficiency of permeate flux than that for the other tests (Fig. 2).

3.3. The results of research with the use of the LEWABRANE®RO B400 HR membrane

The retention coefficient for the undesirable components in geothermal water following the RO process using a PA00416HR(C12) membrane with 50% recovery is slightly worse than that following the RO process using a 30HR440i membrane, except for the concentration of boron, which was reduced by 67.83% (Table 1). The complete removal of hardness was observed: a 99.89% reduction for the process using the PA00416HR(C12) membrane and 99.95% for the test using the 30HR440 membrane. The concentration of sulphate ions was decreased by 99.27% for tests using the PA00416HR(C12) membrane and 99.57% for the RO process using the 30HR440i membrane (Table 1). Also, metasilicic acid retention decreased respectively from 98.36% (30HR440i membrane) to 98.28% for the test using the PA00416HR(C12) membrane. The results after the test using the PA00416HR(C12) membrane with 75% recovery showed that the retention coefficient of the undesirable components in geothermal water is quite similar to the other mentioned processes with 75% recovery of feed water (Table 2). The efficiency of the retention ratio of selected elements: boron (55.84%), total hardness (99.80%), sulphate ions (98.79%) and metasilicic acid (98%) in the reverse osmosis process using a PA00416HR(C12) membrane with 75% recovery is slightly lower than in the process using a BW30FR-400 membrane (Fig. 2).

The desalination processes using the PA00416HR(C12) membrane with 50% and 75% recovery were very effective and proceeded with the smallest decrease in permeate flux with time compared to all other tests (Figs. 1 and 2).

3.4. The results of the process with the use of the AG membrane

Compared to the previously mentioned experiments the efficiency of the retention coefficient of the undesirable components in geothermal water after the process using the AG membrane with 50% recovery is slightly worse, or better, for particular elements, except for the concentration of boron (40.37%) which is significantly lower than for other analyses (with 50% recovery) (Table 1). A similar trend is observed for the test with the use of the AG membrane with 75% recovery, the concentration of boron (46.41%) is also significantly lower than for other analyses. The retention coefficient of total hardness was decreased by 99.92% for geothermal water after carrying out the process using the AG membrane with 75% recovery and 99.91% with 50% recovery. The results of the process, which was carried out to obtain 75% recovery of feed water with the use of the AG membrane, demonstrated that the concentrations of sulphate ions, 99.60%, and metasilicic acid, 97.87%, were somewhat further decreased than with the use of the AG membrane with 50% recovery (respectively 99.39% and 95.51%).

Also, in this case the desalination process of the raw geothermal water proceeded with a significant decrease in permeate flux with time in the test using the AG membrane with 50% recovery (the worst efficiency of permeate flux for all tests with 50% reception) (Fig. 1). The process using the AG membrane with 75% recovery of feed water proceeded with a slight decrease in efficiency of permeate flux (Fig. 2).

4. Conclusions

In the work discussed, the research was directed at optimising the selection of the membrane for the reverse osmosis process to enable proper water treatment. The geothermal water used in the tests exhibits a high content of silica, sulphate ions and a high value of total hardness which can result in a scaling phenomenon occurring. Comparing the retention coefficient for the undesirable components in geothermal water after the tests with the use of different membranes with 50% recovery of feed water, it can be observed that for all the parameters examined the RO process using the BW30HR-440i membrane resulted in a substantially increased efficiency of retention coefficient in comparison with the other membranes, except for the concentration of chlorides, iron and boron (the highest value for the test used the PA00416HR(C12) membrane: 67.83%). A beneficial reduction in the total hardness of the solution, for tests with a 50% recovery, was observed to range from 99.51% for the test using the BW30FR-400 membrane to 99.95% for the test using the BW30HR440i membrane. For tests with 50% recovery, the concentration of sulphate ions decreased by 99.57% for the processes using the BW30HR-440i membrane and 98.54% for the BW30FR-400 membrane. The value of the retention coefficient for metasilicic acid increased from 95.51% for the processes using the AG membrane to 98.36% for the BW30HR-440i membrane. Boron reduction improved from 40.37% for the AG membrane to 67.83% for the PA00416HR(C12) membrane with the same process parameters. The results of the processes which were carried out to obtain a 75% recovery of feed water demonstrated that the greatest reduction in total hardness of solution was obtained for those processes using the BW30FR-400 and PA00416HR(C12) membranes (99.92%). A high retention ratio was achieved for sulphate ions: from 98.45% for the process with the use of the BW30HR-440i membrane to 99.60% for the process with the use of the AG membrane. The value of the retention coefficient of metasilicic acid is within the range, depending on the membrane used, from 97.73% for the process using the BW30HR440i membrane to 98.4% for the test using the BW30FR-400 membrane. Boron reduction improved from 46.41% for the AG membrane to 59.12% for the BW30FR-400 membrane.

The process of desalinating geothermal water using selected membranes with 50% recovery proceeded with a slightly significant decrease in permeate flux with time, which probably indicated that the phenomenon of membrane scaling occurred in all cases. The largest decline in productivity of permeate flux was found in the process using the AG membrane. The lowest loss in efficiency of permeate flux was found in the process using the PA00416HR(C12) membrane. However, the assays of geothermal water using selected membranes with 75% recovery mostly proceeded with a significant decrease in permeate flux with time. The lowest decrease in efficiency of permeate flux was found with the process using the AG membrane. The largest decrease in the productivity of permeate flux was found with the process using the BW30HR-440i membrane.
Acknowledgement

The work presented was financed by the Polish National Centre for Research and Development, grant No 245079 (2014–2017).

References


