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Process of geothermal water treatment by reverse osmosis. The research with antiscalants

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ABSTRACT

One of the main operational problems when using reverse osmosis (RO) technology is membrane scaling. Scaling directly affects membrane service life, the efficiency of the desalination process and operating costs, therefore predicting and preventing sediment precipitation in membrane systems is a key aspect of their operation. This process also plays an important role during the desalination of geothermal waters. Geothermal waters often exhibit high levels of carbonate hardness and elevated concentrations of silica, sulphates, strontium, barium and other elements. The elevated temperature of geothermal water during its desalination is particularly conducive to the formation of sediments, especially carbonates, but also silica, barite, alumino-silicates and in some cases copper sulphates. The work presents the results of research designed to optimise the selection of antiscalants which permit the reduction of deposits precipitating on the membranes used in the process of water treatment. They included modelling studies, laboratory tests and microscopic analysis of sediments formed on the membranes. The study used brackish geothermal water extracted from the geothermal intake. The geochemical modelling that was carried out (using the program PhreeqC) has allowed a detailed assessment of the tendency of mineral deposits to precipitate from the water being tested. It demonstrated what should be expected as regards the precipitation of different geochemical characteristics. It was all the more necessary to propose an appropriate antiscalant for a broad spectrum of action. Several commercially available antiscalants were used for tests in the RO process. The study was carried out using DOW FILMTEC membranes.

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

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1. Introduction

The reverse osmosis process is used in water treatment to remove undesirable material in mineralised waters, and is capable of removing up to 99% and more of the dissolved salts (ions) in the feed water. However, one of the most significant operational problems during the reverse osmosis process is membrane scaling.

Scale formation is a complex phenomenon involving both crystallisation and transport mechanisms. Thermo-

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dynamically, crystallisation or precipitation of calcium carbonate ($CaCO_3$), calcium sulphate ($CaSO_4 \cdot H_2O$), barium sulphate ($BaSO_4$), strontium sulphate ($SrSO_4$), silica (SiO_2), calcium phosphate ($Ca_3(PO_4)_2$) or aluminosilicates (Al_2SiO_5) becomes possible when the activity of ions in solution is above their saturation limit and the solution is supersaturated [1,3,4]. Membrane scaling directly affects its service life, the efficiency of the desalination process and operating costs [1–3,5–7].

The aim of this work is to present the results of research oriented towards optimising the selection of antiscalants which could enable the precipitation of deposits on the reverse osmosis membranes to be reduced. The research has been carried out using geothermal water obtained from the Banska PGP-1 well located in the south of Poland as an example. In a previous paper [8,9] of the geothermal desalination study, the authors showed that high-quality water for potable purposes may be obtained during the desalination of cooled geothermal water. However, it should be noted that geothermal water is often characterised by increased mineralisation, high silica concentration, a high value of total hardness, and elevated concentrations of iron, silica, sulphates and other macro and micronutrients which can induce a scaling phenomenon [1,4,9,10]. In this situation, preventing sediment precipitation in membrane systems is a key aspect of the operation [1].

To minimise the precipitation of deposits on the membrane surface during the desalination process, selected antiscalants were used. Five different commercially available types of antiscalants were chosen [11,12]. The research included all the steps of scaling analysis, from modelling studies, laboratory tests and microscopic analysis of the sediments formed on the membranes. The purpose of the research was to select an appropriate antiscalant for a broad spectrum of action in water treatment, especially in the reverse osmosis process.

2. Method and process technology

2.1. Geothermal water

Raw water from Banska PGP-1 well is characterised by elevated mineralisation (TDS 2.4 g/L), high silica concentration (60 mg SiO_2/L), high value of total hardness (650 mg $CaCO_3$/L) and elevated concentrations of sulphates (855 mg/L), calcium (194 mg/L), magnesium (42 mg/L), boron (10 mg/L) and other macro and micronutrients. According to the Szczukariew-Prikłonski classification, raw water possesses a SO_4-Cl-Na-Ca hydrogeochemical type. The specific chemical and physical compositions of raw geothermal water, and, in addition, raw geothermal water with the addition of various antiscalants, are shown in Table 1. In all tests raw water had a temperature of 22°C.

2.2. Antiscalant types and doses

For these analyses five different commercially available types of antiscalant indexed (Table 2) as: 1) A01, 2) A02, 3) A04; 4) A09 and 5) A520 (which was used in three various doses) were chosen.

The amount of dose for each type of antiscalant was adapted to the water's pH value (Table 1). The dose of antiscalants A01 and A02 applied during these experiments was established at 0.3 mL for 300 mL of used feed geothermal water (1 mL/1 L), while for the tests with addition antiscalants A04 and A09 at 0.2 ml for 300 mL of used feed geothermal water (about 0.7 mL/ 1L) and for antiscalant A520 at 1.8 ml (6 mL/1 L), 3.0 ml (10 mL/1 L) and 3.6 ml for 300 mL (12 mL/1 L) of used feed geothermal water. Each antiscalant is adjusted to prevent membrane scaling and is specially formulated to restrain sediment precipitation on the membrane in water treatment. The antiscalants chosen are customised to use in water with a high concentration of silica, calcium sulphate and calcium carbonate.

2.3. Method used and testing equipment

The tests were carried out on the process efficiency of reverse osmosis. The analyses were conducted using the stirred cell device in dead-end mode, utilising membrane BW30FR-400 DOW FILMTEC, at a stable pressure of 15 bar. The raw water with added antiscalant was placed in a stirred cell under the specified pressure. The stirred dead-end filtration cell was in the shape of a cylinder with an internal diameter of 69.5 mm and a height of 115 mm. The maximum capacity of the cell was 400 mL, while the working volume of raw geothermal water in conducted tests was 300 mL. The active area of the membrane was 35.25 cm^2. The reverse osmosis processes were carried out to obtain 50% recovery of feed water with the time measurement to receive each additional 5 mL of permeate. Each of the new membranes was conditioned by filtration with deionised water to check the efficiency of the membrane and gain the value of the deionised water permeate flux. A schematic diagram of the reverse osmosis process system used in the dead-end mode is shown in Fig. 1. Fig. 2 shows a schematic diagram of the stirred cell device used in the experiments.

2.4. Methodology of physico-chemical analysis

The pH, electrical conductivity (EC) and temperature values of the water containing added antiscalant to be analysed were measured at a laboratory-scale immediately after obtaining water from the system using the electrometric method. Other parameters and inorganic components were specified in an accredited laboratory of the Department of Hydrogeology and Engineering Geology at the AGH University of Science and Technology in Krakow (PCA-AB 1050) using the inductively coupled plasma mass spectrometry (ICP-MS – for determination of Al, PO_4 and Ba ions concentrations) and inductively plasma optical emission spectrometry (ICP-OES – for determination of Na, Ca, Mg, K, Sr, Fe, B, SO_4 and H_2SiO_3 concentrations) methods according to European norms respectively ISO 17294-2:2016 [13] and ISO 11885:2007 [14]. Water alkalinity was measured by titration of water sample by the hydrochloride acid [15] and chloride ion content was determined by titration according to accredited testing procedures based on the Mohr's method [16]. The total phosphorus and sul-

Table 1
Influence of antiscalants type on the Banska PGP-1 geothermal water using a BW30FR-400 Dow Filmtec reverse osmosis membrane (transmembrane pressure 15 bar, R-retention coefficient)

Parameters	Raw geothermal water			Water with A01			Water with A02			Water with A04			Water with A09			Water with A520 (the mean dose)			Water with A520 (the lowest dose)			Water with A520 (the highest dose)		
	Raw water [mg/L]	Permeate [mg/L]	R [%]	Raw water with A01 [mg/L]	Permeate [mg/L]	R [%]	Raw water with A02 [mg/L]	Permeate [mg/L]	R [%]	Raw water with A04 [mg/L]	Permeate [mg/L]	R [%]	Raw water with A09 [mg/L]	Permeate [mg/L]	R [%]	Raw water with A520 [mg/L]	Permeate [mg/L]	R [%]	Raw water with A520 [mg/L]	Permeate [mg/L]	R [%]	Raw water with A520 [mg/L]	Permeate [mg/L]	R [%]
[1]TH	655.40	3.2	99.51	639.90	0.0	100.00	584.4	0.0	100.00	649.6	0.0	100.00	641.9	0.0	100.00	629.4	0.2	99.97	637.10	0.2	99.97	625.10	0.2	99.97
Na^+	488.68	10.73	97.80	470.59	7.42	98.42	602.09	4.18	99.31	474.91	10.37	97.82	494.56	12.22	97.53	719.77	9.06	98.74	637.89	11.26	98.24	766.01	6.91	99.10
K^+	47.64	2.97	93.77	139.58	2.20	98.43	44.63	0.29	99.36	44.73	1.07	97.61	45.11	1.47	96.73	44.21	0.618	98.60	45.37	0.74	98.37	44.02	0.42	99.06
Ca^{+2}	194.10	0.80	99.59	139.44	10.00	94.83	175.48	10.00	94.30	196.46	10.00	94.91	193.53	10.00	94.83	189.84	0.07	99.97	192.67	0.074	99.96	188.94	0.07	99.97
Mg^{+2}	41.58	0.28	99.31	38.22	0.10	99.74	35.63	0.10	99.72	38.751	0.1	99.74	38.657	0.1	99.74	37.847	0.1	99.74	38.012	0.1	99.74	37.356	0.1	99.73
Sr^{+2}	6.244	0.2	96.80	5.865	0.2	96.59	4.971	0.2	95.98	6.039	0.2	96.69	5.972	0.2	96.65	5.889	0.2	96.60	5.991	0.2	96.66	5.835	0.2	96.57
Cl^-	487.9	12.2	97.49	516.1	1.0	99.81	508.9	1.0	99.80	489.0	1.0	99.80	512.8	1.0	99.81	579.5	1.0	99.83	584.2	1.0	99.82	604.8	1.0	99.84
SO_4^{-2}	854.71	12.52	98.54	796.65	1.67	99.79	775.28	2.18	99.72	803.14	2.84	99.65	810.25	4.43	99.45	765.67	1.81	99.76	767.22	2.38	99.69	758.84	1.10	99.86
H_2SiO_3	79.43	1.76	97.78	81.73	1.06	98.70	81.42	0.49	99.40	82.3	1.37	98.34	83.97	1.46	98.26	82.95	0.94	98.87	82.79	1.04	98.74	81.75	0.66	99.19
Al^{+3}	0.008	0.006	30.63	0.010	0.005	50.00	0.01	0.005	50.00	0.01	0.005	50.00	0.01	0.005	50.00	0.01	0.007	30.76	0.01	0.005	50.00	0.01	0.005	50.00
Fe^{+2}	0.232	0.010	95.64	0.147	0.010	93.21	0.016	0.010	35.78	0.149	0.010	93.27	0.103	0.010	90.28	0.119	0.010	91.60	0.111	0.010	90.95	0.162	0.010	93.84
PO_4^{-3}	0.007	0.007	0	310.1284	0.0061	99.99	277.7635	0.0061	99.99	116.1492	0.0061	99.99	305.6133	0.0061	99.99	659.0921	0.0061	99.99	427.9081	0.1641	99.96	788.4214	0.0061	99.99
Ba^{+2}	0.0436	0.0023	94.78	0.0603	0.0005	99.17	0.0410	0.0005	98.78	0.0558	0.0005	99.10	0.0488	0.0005	98.98	0.0576	0.0005	99.13	0.0546	0.0005	99.08	0.0557	0.0005	99.02
B	9.76	3.71	61.99	9.06	2.71	70.10	9.15	1.57	82.84	9.25	3.07	66.81	9.32	2.92	68.67	9.18	2.64	71.24	9.22	3.05	66.92	9.08	2.81	69.05
EC [mS/cm]	3.35	0.088	97.37	3.660	0.0492	98.66	3.830	0.0246	99.36	3.440	0.0598	98.26	3.460	0.0734	97.88	4.050	0.0497	98.77	3.085	0.0595	98.45	4.150	0.0411	99.01
pH	6.80	6.55	–	5.75	5.71	–	6.98	6.12	–	5.71	5.28	–	5.40	5.19	–	5.93	5.68	–	6.07	5.39	–	5.91	5.58	–

[1] Total hardness in mg $CaCO_3$/L

Table 2
Antiscalant types (after product cards)

Antiscalant Typed	Dose [mL/L]	Preventing *Sulphates* Scale	Preventing *Carbonates* Scale	Preventing *Silicates* Scale
A01	0.1	√	√	—
A02	0.1	√	√	—
A04	0.7	√	√	√
A09	0.7	—	—	√
A520	6	—	√	√
	10			
	12			

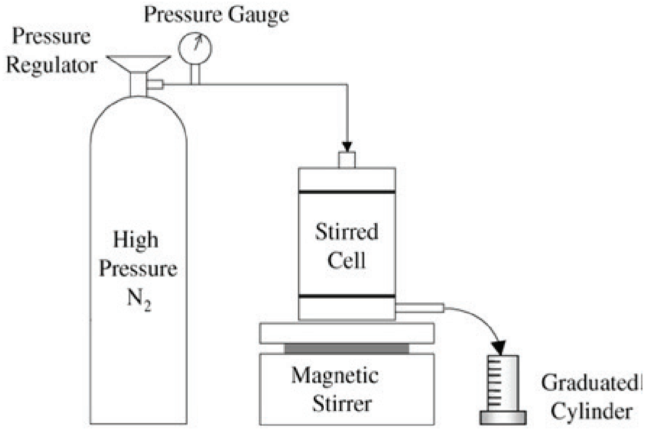

Fig. 1. Diagram of the system for carrying out reverse osmosis in dead-end mode.

phur were measured respectively using ICP-MS and ICP-OES method and their concentrations were recalculated to phosphate and sulphate ions. The methods were validated for those purposes.

2.5. Scaling prognosis – modelling

An estimate of the scaling process was developed using a geochemical modelling program -*Phreeqc Interactive 3.3.3-10424* (PHREEQCI – Wateq4f minerals database) [17]. The scaling phenomenon was calculated based on the physicochemical composition of raw water and raw water with a particular antiscalant, pH value and temperature of feed water, including a 15 bar transmembrane pressure during the reverse osmosis process. It has enabled a detailed prognosis of the tendency of mineral deposits to precipitate from the water being tested and has also demonstrated what should be expected due to the precipitation of sediments with different geochemical characteristics.

2.6. Membrane scaling assay – methodology

The morphology and chemical composition of the mineral components of the materials identified on the membrane were determined in micro scale using the electron scanning microscope (SEM). A FEI Qanta 250 FEG scanning microscope equipped with an additional chemical composition analysis system based on energy dispersion scattering – the EDS EDAX equipment was used to make this analysis.

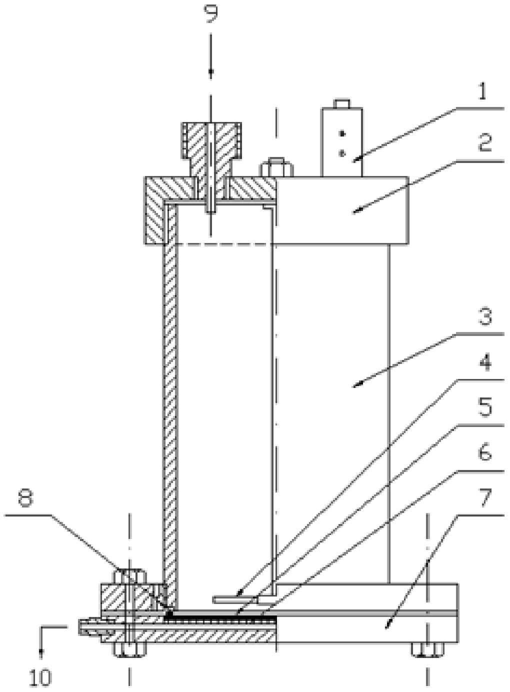

Fig. 2. Schematic diagram of the stirred cell device used in the reverse osmosis process (Explanation: 1-safety valve; 2-top cover; 3-pressure cylinder; 4-magnetic stirrer; 5-membrane; 6-perforated plate; 7-lower cover; 8-gasket; 9-gas supply; 10-permeate discharge).

3. Results and discussion

As a first step in the research, geothermal water from the Bańska PGP-1 well without any antiscalants was subjected to the reverse osmosis process and, in a second step, water with antiscalant was analysed in dead-end mode.

3.1. The results of raw geothermal water treatment without antiscalant

The results of the research performed on the selected physicochemical parameters of raw geothermal water are shown in Table 1. From the research conducted it was shown that there was a high degree of rejection of undesirable constituents, with the exception of the boron ion (61.99%), which is the result of the pH value of the feed water. Numerous pieces of research on the efficiency of removal of boron ions from water and wastewaters in the reverse osmosis process demonstrate that a high retention rate for boron, at a level exceeding 98%, is possible in water with a pH value of at least 10 [8,18–21]. The results obtained from the geochemical modelling revealed that for raw geothermal water the supersaturated state of the solution tested and the tendency to precipitate give rise to the following minerals (Table 3,

Table 3
Estimated levels of scaling – results of modelling

Type of water	Supersaturation State	Equilibrium state	Undersaturation State
Raw geothermal water	$BaSO_4$,SiO_2, $FeOOH$,Fe_2O_3,$Al(OH)_3$,$Al_2Si_2O_5(OH)_4$	$CaCO_3$, $CaMg(CO_3)$	$CaSO_4$, $Ca_5(PO_4)_3OH$
Water + A01	$BaSO_4$,SiO_2,$FeOOH$, Fe_2O_3, $Al(OH)_3$, $Al_2Si_2O_5(OH)_4$,$Ca_5(PO_4)_3OH$	—	$CaSO_4$, $CaCO_3$, $CaMg(CO_3)$
Water + A02	$BaSO_4$,SiO_2, $FeOOH$,Fe_2O_3,$Al(OH)_3$, $Al_2Si_2O_5(OH)_4$,$Ca_5(PO_4)_3OH$	—	$CaSO_4$, $CaCO_3$, $CaMg(CO_3)$
Water + A04	$BaSO_4$,SiO_2, $FeOOH$,Fe_2O_3,$Al(OH)_3$, $Al_2Si_2O_5(OH)_4$,$Ca_5(PO_4)_3OH$	—	$CaSO_4$, $CaCO_3$, $CaMg(CO_3)$
Water + A09	$BaSO_4$,SiO_2, $FeOOH$,Fe_2O_3,$Al(OH)_3$, $Al_2Si_2O_5(OH)_4$,$Ca_5(PO_4)_3OH$	—	$CaSO_4$, $CaCO_3$, $CaMg(CO_3)$
Water + A520	$BaSO_4$,SiO_2, $FeOOH$,Fe_2O_3,$Al(OH)_3$, $Al_2Si_2O_5(OH)_4$,$Ca_5(PO_4)_3OH$	—	$CaSO_4$, $CaCO_3$, $CaMg(CO_3)$

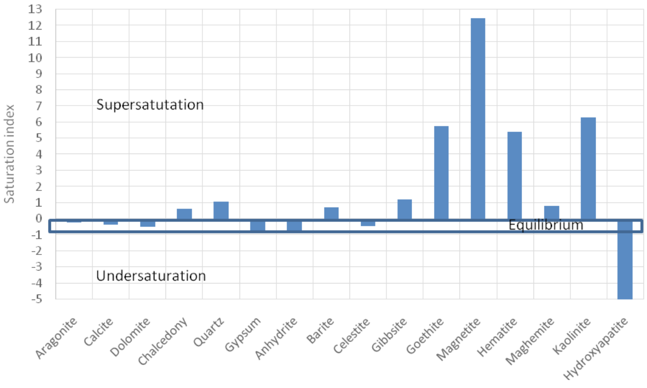

Fig. 3. The values of saturation indices for each solid phase.

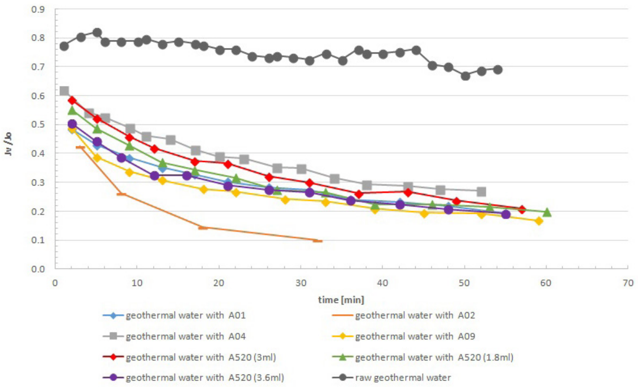

Fig. 4. Changes of permeate flux during the reverse osmosis of geothermal water and geothermal water with the addition of selected antiscalants, using the BW30FR-400 membrane.

Fig. 3): sulphates – barite ($BaSO_4$), silicates – chalcedony and quartz, iron oxides and hydroxides – goethite ($FeOOH$), hematite (Fe_2O_3), maghemite (Fe_2O_3), magnetite (Fe_3O_4), aluminium hydroxide – gibbsite ($Al(OH)_3$) and also aluminium silicate forms – kaolinite ($Al_2Si_2O_5(OH)_4$) and others. In a state of equilibrium with the solution are: aragonite, calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$). Calcium sulphate – gypsum ($CaSO_4$), calcium sulphate – anhydrite ($CaSO_4$) and hydroxyapatite are in a state of under saturation with the solution. The values of supersaturation indices for each solid phase as predicted by the thermodynamic code have been provided in Fig. 3.

The process of desalination of raw geothermal water proceeded in a stable manner, but with a slight decrease in permeate flux with time. The changes in permeate flux are shown in Fig. 4.

The membrane used in the study was subjected to further analysis to identify the mineral deposits on the surface thereof. A photomicrograph of the membrane obtained from an electron scanning microscope is shown in Fig. 5. The experiment with raw geothermal water was conducted until obtain 50% recovery of feed water. Time to gain such an amount of water was measured at approximately less than 60 min. For the tests with addition selected antiscalants such a time was needed to obtain about 20–30% recovery of feed water. The effectiveness of the filtration was evaluated by the determination of transport properties of the membrane using volumetric permeate flux measurements in time, on the basis of which relative permeate flux (J_i/J_0, J_0 – volumetric flux of deionized water, J – volumetric flux of permeate) was established.

Individual concentrations of deposits represented by silicate minerals, and also by oxides and hydroxides of iron and aluminium, were found on the membrane surface in the microscope images (Fig. 5a). Deposits of carbonate minerals, including aragonite and dolomite, are also trace-

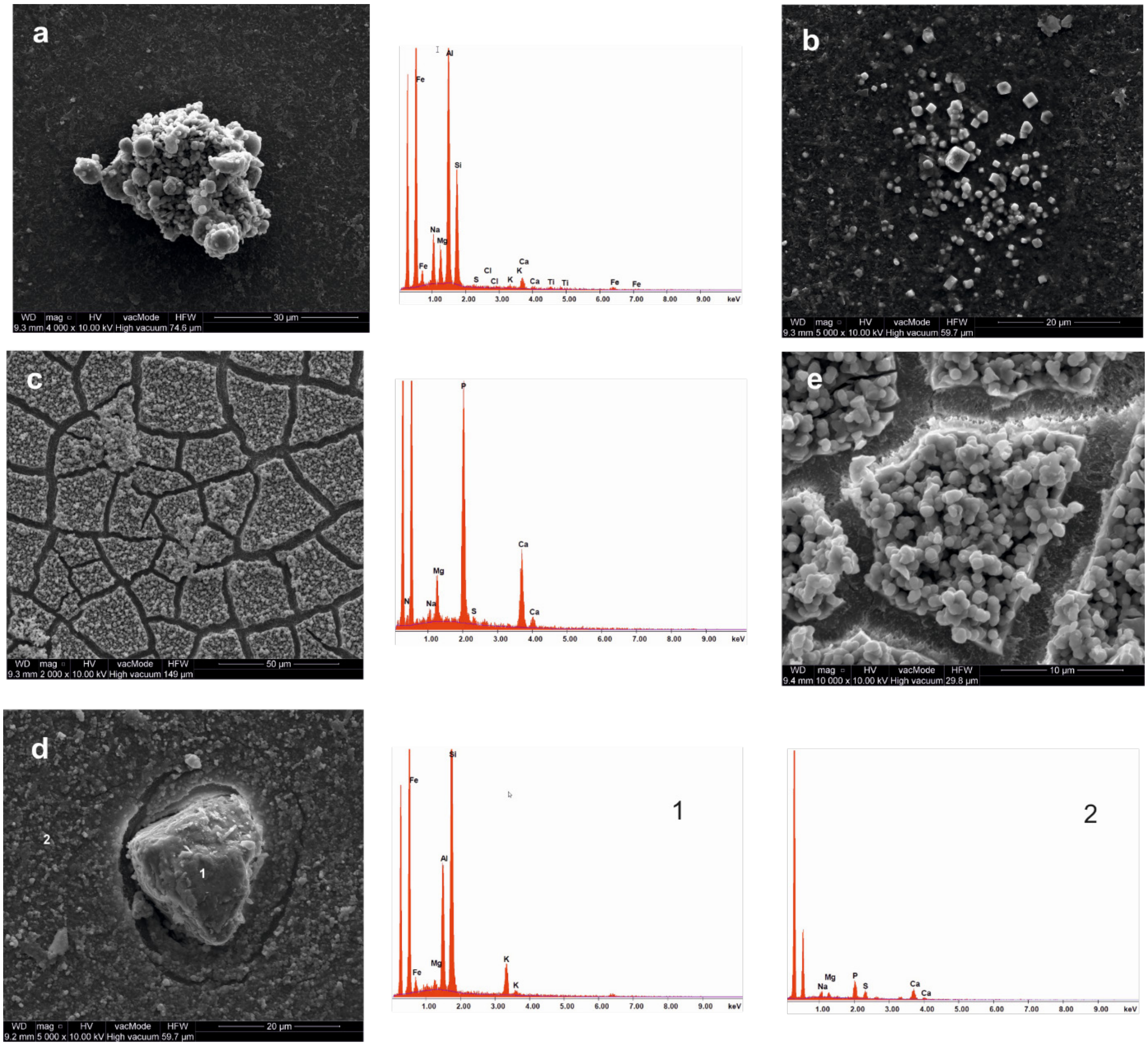

Fig. 5A. SEM-EDS image of the BW30FR-400 membrane surface in membrane autopsy (after treating raw geothermal water and water with A01–A09 antiscalants). Explanations: a) silicate minerals, oxides and hydroxides of iron and aluminium; b) halite; c) phosphate minerals (probably apatite/hydroxyapatite (magnification 2 000x); d) siliceous minerals and also oxides and hydroxides of iron and aluminium (1), probably apatite (2); e) phosphate minerals (probably apatite/hydroxyapatite (magnification 10 000x)

able, but on a smaller scale. However, no precipitation of sulphate minerals was found. Deposits of chlorides (the result of halite precipitation from the water remaining on the membrane) (Fig. 5b) were also observed.

One should be noticed that the supersaturation index on membrane surface is higher compared to that estimated for bulk fluid. This statement could justify the fact that in some cases salts in under saturation state were observed on membrane surface.

3.2. Raw geothermal water with the addition A01

A01 used in the reverse osmosis test is a liquid formulation based upon a blend of phosphonates, which are effective in preventing scale formation on the membrane surface (*Veolia product card*). It is efficient and appropriate in protecting against sulphate and carbonate scales (Table 2). The results of the research performed on the selected physicochemical parameters for raw geothermal water with the addition of A01 are shown in Table 1.

The efficiency of the retention coefficient of the undesirable components in raw water with the addition of A01 is slightly better (about 10% higher) than in the process with raw water alone (without antiscalant), except for the concentration of calcium, strontium and iron. A beneficial reduction in total hardness of the solution was observed: 100% for raw water with the addition of A01 and 99.51% for raw water. The concentration of sulphate ions was decreased by 99.79% for raw water with the addition of A01 and 98.54% for raw water. The value of the retention coefficient for metasilicic acid increases from 97.78% in raw water to 98.7% in raw water with the addition of A01.

The desalination process of the raw geothermal water with A01 proceeded with a significant decrease in permeate flux with time, which indicated that the phenomenon of membrane scaling was occurring (Fig. 4). The results obtained from the geochemical modelling of geothermal feed water with A01, revealed the same state of saturation as for raw geothermal water alone. An exception was seen with aragonite, calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$) which weren't identified and also in connection with increased saturation in the hydroxyapatite solution, whose state changed from under saturated to supersaturated (increased tendency to precipitate) (Table 3). A recognized tendency of secondary minerals to precipitate from the solution was confirmed by the results of the research on microscope images of the membranes. Generally, the entire surface of the membrane was covered with a coating built up of deposits with phosphate minerals (probably apatite/hydroxyapatite) (Fig. 5c). Minor inclusions of other precipitates are only observed in individual microregions (Fig. 5d). Intensive membrane scaling has contributed to a sharp decline in the efficiency of the process of reverse osmosis. The effect obtained had the opposite character to that expected. As a result of an intense reaction between the calcium and magnesium ions occurring in the geothermal water and with the active substance in the A01antiscalant, a deterioration of membrane filtration conditions occurred.

3.3. Raw geothermal water with the addition A02

A02 used in the reverse osmosis test is a nontoxic liquid formulation based upon phosphonates, which effectively prevent scale formation on the membrane surface (*Veolia product card*). It is efficient and appropriate against sulphate and carbonate scales. On account of its characteristics, antiscalant A02 has the same uses as A01.

The results of the research carried out on the selected physicochemical parameters of raw geothermal water with the addition A02 are shown in Table 1. The retention coefficient of the undesirable components in geothermal water with the addition of A02 is also slightly improved compared to the process with raw water, apart from the concentration of calcium, strontium and iron, like in the test with A01. The total hardness reduction was observed to be 100% for water with A02 and 99.51% for the first test with raw geothermal water. The concentration of sulphate ions was decreased by 99.72% for water with A02 and 98.54% for geothermal water. In addition, metasilicic acid retention increased respectively from 97.78% to 99.4% in water with the addition of A02. For iron the retention coefficient decreases to a very low value: 35.78% (Table 1). The desalination process proceeded with a significant decrease in permeate flux with time which is presented in Fig. 4.

An analysis of the estimates of the precipitation of minerals from solution, obtained from the modelling, revealed the same state as in the above mentioned test with A01 (Fig. 5c). As a result of dosing the feed with antiscalant, the phosphate ion content in the feed increased from 0.007 mg/L to greater than 277 mg/L (Table 1). On the other hand, the physicochemical properties of the geothermal water examined resulted in a very intensive precipitation of phosphate minerals and a reduction in permeate flux over time (Fig. 4).

3.4. Raw geothermal water with the addition A04

A04 used in the reverse osmosis test is a nontoxic liquid formulation based on phosphonates and dispersants, which is effective in preventing scale formation on membrane surfaces (*Veolia product card*). It is efficient and appropriate against sulphate, silica and carbonate scales.

The efficiency of the retention coefficient of the undesirable components in water with A04 is also slightly better compared to processing with raw geothermal water, except for the concentration of sodium (97.82%), calcium (94.91%) and iron (93.27%). Beneficial reduction in the total hardness of the solution was observed: 100% for raw water with the addition of A04 and 99.51% for raw water. The concentration of sulphate ions was decreased by 99.65% for raw water with the addition A04 and 98.54% for raw water. The value of the retention coefficient of metasilicic acid increased from 97.78% in raw water to 98.34% in raw water with the addition of A04.

Also, in this case, the desalination process of the raw geothermal water proceeded with a considerable decrease in permeate flux with time. The changes in permeate flux are shown in Fig. 4.

Based on the physicochemical composition, temperature, and the pH value of the feed water with the addition of A04 and taking into account the input parameters, the scaling results predicted from the modelling results revealed the same state of saturation for the individual mineral forms examined as for the process of raw geothermal water, with the exception of aragonite, calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$) which weren't identified, and also in connection with increased saturation in the hydroxyapatite solution, whose state had changed from undersaturated to supersaturated (increased tendency to precipitate) (Table 3). In the SEM image of the membrane after tests, a coating build-up of precipitated deposits of phosphates (probably apatite and hydroxyapatite) was also observed. Precipitates of siliceous minerals and also oxides and hydroxides of iron and aluminium (Fig. 5d) may locally be found on the surface of this cover of the membrane.

3.5. Raw geothermal water with the addition A09

A09 used in the reverse osmosis test is a nontoxic liquid formulation based upon a blend of phosphonates which effectively prevents scale formation on the membrane surface (*Veolia product card*), especially for water with a high silica content. It is efficient and appropriate against a wide range of scales and fouling.

As in the previously mentioned experiments, the retention coefficient of the main undesirable components was slightly better in water with A09 compared to processing with raw geothermal water (Table 1). However, the desalination process proceeded with a significant decrease in permeate flux with time. The geochemical modelling of the degree of saturation of the feed dosed with the antiscalant

A09 demonstrated the same state of saturation for the individual mineral forms examined as for the processing of waters with the other mentioned antiscalants. The water desalination process using the A09 antiscalant demonstrated that the surface of the membranes was covered almost exclusively with fine-grained phosphate minerals compounds (probably apatite/hydroxyapatite) (Fig. 5e). These phosphates cover essentially the entire surface of the membranes.

3.6. Raw geothermal water with the addition A520 antiscalant

A520 antiscalant used in the reverse osmosis test is adjusted to high concentrations of silica. A520 is also customized to act as an effective prevention of scale formation on the membrane surface and also to allow one to obtain favourable parameters in the permeate. It is efficient and appropriate against membrane scaling and allows one to use the RO process without previous softening (*Product Card*)

The tests with the usage of A520 antiscalant were conducted in three different doses: the lowest (6 mL/L), mean (10 mL/L) and highest (12 mL/L) (Table 2). The results of the research performed on the selected physicochemical parameters for raw geothermal water with addition of A520 antiscalant in three doses are shown in Table 1.

The efficiency of the retention coefficient of the undesirable components in raw water with the addition A520 antiscalant in three different doses are also slightly better (it appears that the average dose produces the best retention) compared to processing with raw geothermal water, except for the concentration of strontium and iron. A beneficial reduction in the total hardness of solution was observed: 99.97% for raw water with the addition of three different doses of A520 and 99.51% for raw water. The concentration of sulphate ions was decreased by 99.69% for raw water with the addition of the lowest dose of A520, 99.76% with the addition of the mean dose of A520, 99.86% with the addition of the highest dose of A520 and 98.54% for raw water. The value of the retention coefficient of metasilicic acid increases from 97.78% in raw water to 98.74% in raw water with the addition of the lowest dose of A520, 98.87% with the addition of the mean dose of A520 and up to 99.19% with the addition of the highest dose of A520. The efficiency of the retention coefficient of boron in the reverse osmosis process with raw water with the addition A520 in three doses is slightly higher than the process with raw water (61.99%), the highest value is achieved for the mean dose of A520 (71.24%).

The desalination process of the raw geothermal water also proceeded with a significant decrease in permeate flux with time, which indicated that a membrane scaling phenomenon had occurred (Fig. 4). The results of the geochemical modelling in three doses of antiscalant indicated the same degree of saturation for the individual mineral forms examined as for the process of treating raw geothermal water, with the exception of aragonite, calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$) which weren't identified and also in connection with increased saturation in the hydroxyapatite solution whose state has changed from undersaturated to supersaturated (increased tendency to precipitate) (Table 3).

The membranes used in the study were subjected to further analysis to identify the mineral deposits on the surface thereof. Photomicrographs of membranes obtained from the electron scanning microscope are shown in Fig. 6. In the case of all three doses of antiscalant used, a coating composed of crystallised sulphate and phosphate minerals was found on the surface of the membrane. On this coating, covering practically the entire surface of the membrane, superstructures of deposits of siliceous minerals occur with a succeeding superstructure of minerals from the phosphate group (Fig. 6).

In the case of all three doses of antiscalant used, a coating composed of crystallised sulphate and phosphate minerals was found on the surface of the membrane. On this coating, covering practically the entire surface of the membrane, superstructures of deposits of siliceous minerals occur with a succeeding superstructure of minerals from the phosphate group (probably apatite) (Fig. 6).

4. Summary and Conclusions

In the work presented here, the research was directed to optimising the selection of antiscalants for the reverse osmosis process to enable the reduction of precipitate deposits on the membranes used in the process of water treatment. The geothermal water used in the tests has a high silica and sulphate ion content and a high value of total hardness, which can cause a scaling phenomenon to occur. In this case, in order to minimise the precipitation of deposits on the membrane surface several commercially available antiscalants were applied. An estimate of the degree of scaling was made for all the processes examined using geochemical modelling based on the physicochemical composition, temperature, and pH value of the feed water with the addition particular antiscalants and taking into account their input parameters. Comparing the retention coefficient of the undesirable components in raw water with the addition of selected antiscalants, it can be observed that usage of antiscalants resulted in a substantial increase in the efficiency of the retention coefficient for all the parameters examined, except for the concentration of sodium, calcium, iron and strontium. The beneficial reduction in total hardness of the solution was observed from 99.68% for raw water with ions to 100% for raw water with A01, A02, A04 or A09 (99.51% for raw water). A high retention coefficient was achieved for sulphate ions: from 99.45% for raw water with A09 to 99.86% for raw water with the highest dose of A520 (98.54% raw water). The value of the retention coefficient of metasilicic acid depends on the antiscalant applied and is within the range from 98.26% in raw water with A09 to 99.4% in raw water with A02. However, the process of desalination of raw geothermal water with the addition of selected antiscalants proceeded with a significant decrease in permeate flux with time, which indicated that the membrane scaling phenomenon occurred in all cases. The largest decline in productivity of the permeate flux was obtained for the process with the addition of the antiscalant A02. The lowest loss in efficiency of permeate flux was obtained in the process with the addition of the antiscalant A04.

The results of the geochemical modelling for water with particular antiscalants revealed the same state of sat-

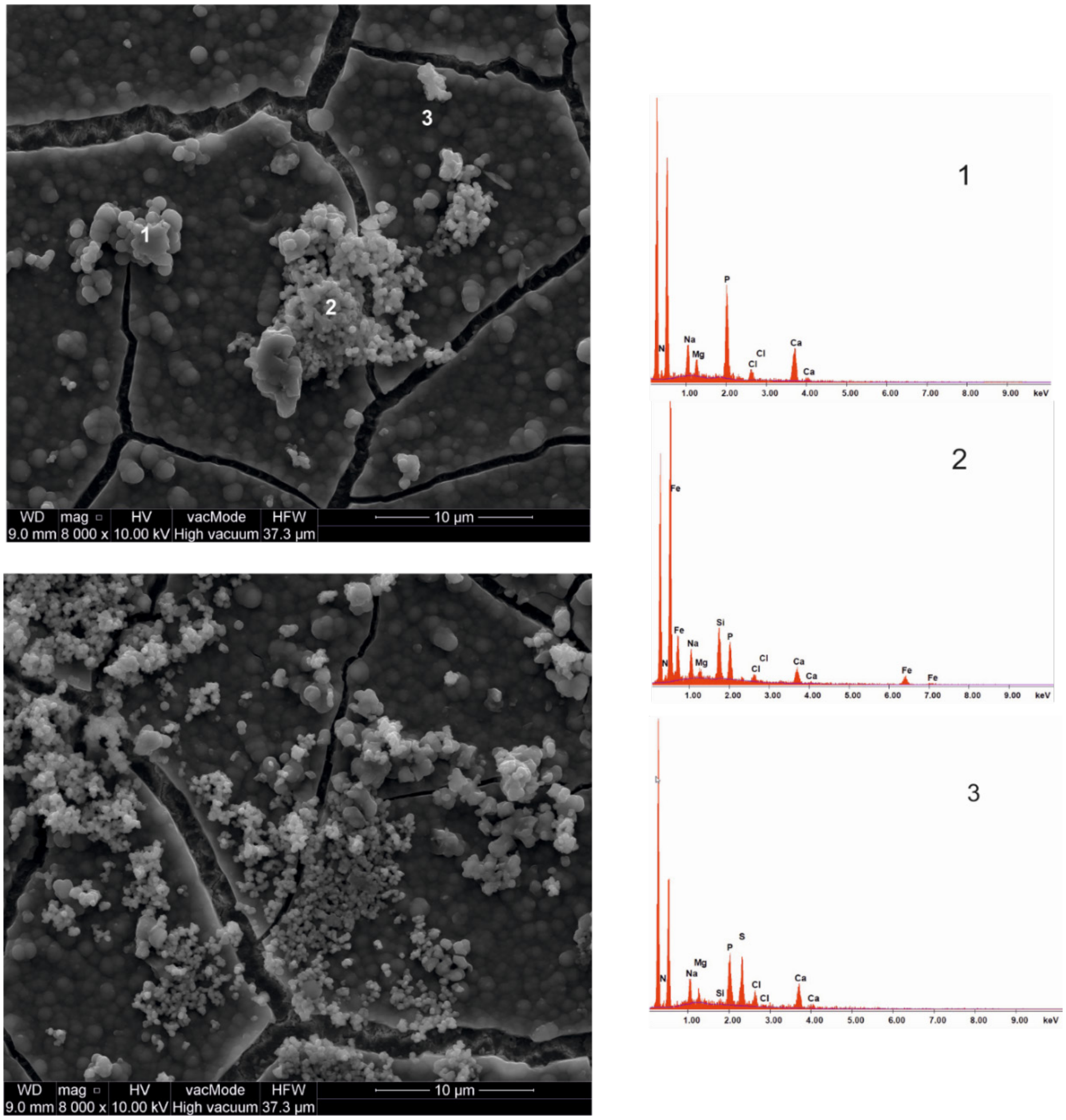

Fig. 6. SEM-EDS image of the BW30FR-400 membrane surface in membrane autopsy (after treating the geothermal water with A520 antiscalants). Explanations: 1) minerals from the phosphate group (probably apatite); 2)siliceous minerals; 3) sulphate and phosphate minerals.

uration for the individual mineral forms examined as for the process of raw geothermal water, with the exception of aragonite, calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$), which weren't identified. Based on the modelling, it was found that, for tests with A01, A02, A04 and with three doses of A520, saturation of the hydroxyapatite in the solution increased and its state changed from undersaturated to supersaturated (increased tendency to precipitate). This effect was achieved as a result of a significant increase in the concentration of phosphate ions in the feed. As a consequence of the reaction with ions occurring in the natural, mineralised geothermal water, at elevated temperature (22°C) and pressure (15 bar), favourable conditions arose for the precipitation of phosphate minerals (probably apatite/hydroxyapatite) from the water on the surface of the membrane. This process contributed to the coverage of practically the whole surface of the membrane with a layer which blocked the flow of water in the RO process.

The studies conducted unambiguously show that the use of an antiscalant produced from phosphonates and dispersants is unjustified in applications related to the desalination of mineralised geothermal waters.

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