



Use of numerical modelling in the prediction of membrane scaling. Reaction between antiscalants and feedwater



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ABSTRACT

Empirical equations and numerical modelling methods are used to predict the possibility of sediments precipitating on the membrane used during the reverse osmosis process. The use of empirical formulae allows approximations to be made of the trends which can exist on the surface of the membrane during the water treatment process. The use of numerical modelling enables more accurate forecasting to be made of precipitation phenomena because it takes into account the process parameters (pressure and temperature) and a detailed identification of the physicochemical properties of feedwater. The modelling of phenomena associated with the prediction of membrane scaling should also be carried out for water to which doses of selected antiscalants have been added. These products activate chemical reactions on the surface of the membrane giving rise to new, different mineral forms causing a decrease in membrane effectiveness. In this paper, the results of comprehensive research and analysis carried out on selected waters are presented. They include forecasting by the use of empirical formulae and thermodynamic models. The results of these predictions were verified on the basis of actual laboratory tests and microscope-based studies of sediments secondarily produced on the reverse osmosis membranes. The research results demonstrate the existence of reactions determined by the physicochemical properties of the antiscalants and the water subjected to a water treatment process.

1. Introduction

Membrane processes, inter alia the reverse osmosis (RO) process, are used as a water treatment to remove undesirable content in water which is characterised by increased mineralisation. By means of reverse osmosis it is possible to remove up to 99% or more of the dissolved ions, particles, colloids, organics, bacteria and pyrogens from water [1,2]. In recent years, membrane processes have been considered as one of the most promising methods for the desalination of geothermal water and producing water which could possibly be used for drinking purposes [3–7]. Notwithstanding the fact that the waters being considered often exhibit high concentrations of silica, sulphates, calcium, magnesium, strontium, barium and carbonate which may affect the membrane's useful life and effectiveness during desalination, membrane processes are widely adopted to permit the utilisation of geothermal waters [8,9]. Scaling phenomena which can occur during, for example, the reverse osmosis process are complex processes involving the crystallization or precipitation of minerals [10–12]. The crystallization or precipitation of calcium carbonate, calcium sulphate, barium sulphate, strontium sulphate, silicates, calcium phosphate or aluminosilicates becomes

thermodynamically possible when the value of the activity of specific ions in the solution is above their saturation limit [10]. Membrane scaling directly affects the efficiency of the process being carried out by flux decline and the available surface area can increase the precipitation of carbonates [10–13]. Conditions of supersaturation can be considered the driving force, which can possibly initiate the crystallization or precipitation of selected minerals [14]. To avoid this problem, the feed water is normally dosed with antiscalants during the membrane process [15–17]. In real life, scale deposition cannot be completely avoided even when antiscalants are used and hence mechanical and chemical cleaning is often applied to clean the fouled parts of the membrane [18,19]. The possibility of predicting the occurrence of scaling phenomena is therefore a key consideration. The Langelier Saturation Index is used to assess the propensity of calcium carbonate to foul the membrane. This is purely based on the solubility product of calcite, the least soluble form of calcium carbonate of its three polymorphs, but more soluble forms such as aragonite can also have an important role in the scaling phenomenon [20–22]. Empirical equations and numerical modelling methods are used to predict the possibility of the precipitation of sediments on the membrane used during the reverse

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osmosis process. The use of empirical formulae allows an approximate assessment to be made of the trends which can exist on the surface of the membrane during the water treatment process. The use of numerical modelling permits more accurate forecasting of the precipitation phenomena because it takes the process parameters (pressure and temperature) and a detailed identification of the physicochemical properties of the feed water into account.

The aim of this work is to present the results of a comprehensive programme of research and analysis carried out on selected waters with and without added antiscalant. The research included all steps of the analysis, from laboratory tests on selected waters to forecasting the possibility of the occurrence of the scaling phenomenon with the use of empirical formulae and thermodynamic models. The results of these predictions were verified by actual laboratory tests and through microscope-based studies of the secondary sediments produced on the membranes used in the reverse osmosis process.

2. Materials and methods

2.1. Geothermal waters

Two natural geothermal waters (GT1 and GT2) were used in the research in two different variants: 1) as raw geothermal water and 2) as raw geothermal water with antiscalant.

2.2. Method of physicochemical analysis

All analyses were performed in the certified Hydrogeochemical Laboratory of the Hydrogeology and Engineering Geology Department of the University of Science and Technology in Cracow (PCA certificate, No. AB 1050). The laboratory takes part in proficiency testing and inter-laboratory comparisons obtaining satisfactory results (Z-score absolute value lower than 2) and has implemented an internal quality control system. All analytical methods used for the determination of the chemical composition of the waters analysed are recommended for this purpose [23,24]. The basic parameters of these methods are summarised in Table 1.

2.3. Methodology of producing scaling forecasts

The scaling forecast was estimated using 1) empirical methods and 2) hydrogeochemical modelling with the PHREEQC program (*Phreeqc Interactive 3.3.3-10424* and *Wateq4f* minerals database) [26]. Two

Table 1
Characteristics of methods used for the determination of chemical composition of analysed waters.

Parameter	Analytical method	Limit of quantification [mg/L]	Related expanded uncertainty [%] (k = 2, 95%)
Cl ⁻	Titration (Mohr method) PN-ISO 9297:1994	1.0	5
HCO ₃ ⁻	titration PN-EN ISO 9963-1:2001 + Ap1:2004	24	5
Ca	Inductively coupled plasma	10	12
Fe	optical emission	0.01	12
K	spectrometry (ICP-OES) PN-EN ISO 1885:2009	0.2	12
Li		0.005	12
Mg		0.1	12
Na		0.1	12
S		1	12
Si		0.1	12
Sr		0.2	12
Al	Inductively coupled plasma	0.005	15
Ba	mass spectrometry (ICP-MS)	0.0005	13
P	PN-EN ISO 17294-2:2006	0.002	14

empirical formulae, the Ryznar Stability Index (RSI) and Langelier Saturation Index (LSI), have been used as a method of prediction of the tendency to form calcium carbonate precipitates in the waters being tested. The RSI and the LSI are equilibrium models which are based on the theoretical concept of saturation and provide an indication of the degree to which the water examined is saturated with calcium carbonate [27]. LSI is a qualitative index which indicates whether the water is undersaturated with respect to calcium carbonate (negative value of LSI) and is potentially corrosive, or whether it is supersaturated with CaCO₃ (positive value of LSI) and has the potential to form scale [28,29]. The tendency to develop calcium carbonate scale during the membrane processes can be approximated by calculating the Langelier Saturation Index [27]:

$$LSI = pH - pH_s$$

where: pH – measured pH value; pH_s – saturation pH for calcium carbonate.

The formula for pH_s is [27]:

$$pH_s = -\log \left(\frac{K_a \cdot \gamma_{Ca^{2+}} \cdot [Ca^{2+}] \cdot \gamma_{HCO_3^-} \cdot [HCO_3^-]}{\gamma_{H^+} \cdot K_{sp}} \right)$$

where: γ_{H^+} – activity coefficient for hydrogen ion; $\gamma_{CO_3^{2-}}$ – activity coefficient for carbonate; $\gamma_{Ca^{2+}}$ – activity coefficient for calcium; [Ca²⁺] – concentration of calcium; [HCO₃⁻] – concentration of bicarbonate; [CO₃²⁻] – concentration of carbonate; K_a – equilibrium constant of equitation (HCO₃⁻)_{aq} ↔ (H⁺)_{aq} + (CO₃²⁻)_{aq}; K_{sp} – equilibrium constant of equitation (Ca²⁺)_{aq} + (CO₃²⁻)_{aq} ↔ (CaCO₃)_s.

Langelier suggested that result of the formula based on the difference between measured pH value of the water under analysis and value of hydrogen ions activity in the saturated calcium carbonate solution, can be used to estimate the tendency of water to form scale. Whereas, the Ryznar Stability Index, which gives an indication about scale and corrosion potential of the water is calculated by the following formula [27]:

$$RSI = 2 \cdot pH_s - pH$$

The PHREEQC program is used to estimate various hydrogeochemical processes, including the equilibrium between water and minerals. To evaluate the occurrence of the scaling phenomenon, the results of physicochemical analyses of geothermal water with and without antiscalant addition were used as input parameters to the SOLUTION_SPECIES in the PHREEQC program. This formula defines both chemical reaction, log K, and the thermodynamic data for each aqueous species. The Saturation Index (SI) of the solution for selected minerals was calculated from the activities of the dissolved species: simple ions, ionic pairs and complexes. The value of the saturation index (SI) is used in order to estimate the saturation state (equilibrium, undersaturation and supersaturation) of each mineral on the basis of a report obtained from the PHREEQC program. When SI = 0, the mineral being examined is in thermodynamic equilibrium between the mineral and the solution. It is also assumed that in natural conditions the phenomenon of polarisation of concentration on the membrane is observed [30]. In the equilibrium state of solution identified by geochemical modelling in respect of the particular mineral, precipitation of sediments may already occur in the actual conditions in which the process of reverse osmosis is carried out. The equilibrium state between water and a mineral corresponds to SI values ± 5% log K (SI = 0 ± 0.05 log K). This range is also applied for hydrogeochemical modelling. SI values above and below 0 correspond to the states of supersaturation and undersaturation respectively. The state of supersaturation implies a tendency of a particular mineral to precipitate from water and a state of undersaturation implies a tendency of a specified mineral to dissolve and the transition of its components from reservoir rock to water [26,31].

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