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Assessment of the influence of temperature and pressure on the prediction of the precipitation of minerals during the desalination process

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ABSTRACT

The results of research designed to examine the influence of the temperature of geothermal water and transmembrane pressure on the precipitation of selected minerals during the desalination process are presented. The geothermal water used in tests was characterised by a high conductivity value, high total hardness and elevated concentrations of sulphates, silicates, calcium, magnesium, and macro and micronutrients, which can cause scaling phenomena to occur. Based on the physicochemical composition of the water, an estimate was made of the extent of the scaling phenomena for all the processes examined. For these analyses, two parameters of the desalination process: 1) the temperature of feed water (T) and 2) the transmembrane pressure (p) were chosen and tested in different value ranges. The research results demonstrate the existence of reactions determined both by hydrogeochemical modelling and from the results obtained during real laboratory tests. It was found that in the case of carbonate (aragonite and calcite) and all silicate minerals, an increase in the pressure value to 40 bar slightly decreases the *Saturation Index* for each mineral. A reverse relationship was reported with gypsum. Increasing transmembrane pressure to 40 bar increases the tendency of the mineral form studied to precipitate.

1. Introduction

In recent years, the desalination of geothermal water using membrane processes has been considered as one of the potential solutions for water reuse [1–3]. However, due to the low solubility of hardness salts and depending on the process parameters used in membrane separation systems, secondary minerals may precipitate from treated water on the membrane surface [4–5]. Various operating conditions such as pH, temperature, transmembrane pressure, permeation rate, flow velocity, and the presence of other salts or metal ions can have an influence on scale formation. Crystallization or precipitation of carbonate, silicate, sulphate or other minerals can occur if the activity of specific ions in solution is above their saturation level (supersaturated) [5–7]. Some precipitation may continue to occur during processes (including membrane processes), unless the precipitation is chemically prevented. The available surface area in the membrane process can enhance the precipitation of calcium carbonate solids and cause a decline in permeate flux [8]. Supersaturation conditions can be considered as a driving force for initiating crystallization of silicate, carbonate and sulphate minerals [9]. Use of the nanofiltration (NF) process as a pre-treatment for desalination processes can potentially be a promising solution [10–12]. Kaya et al. [10] showed, on the basis of a mini, pilot-scale membrane desalination system in Urla, that the use of a NF process as pre-treatment for desalination can contribute to such benefits as 1) reducing the scaling phenomenon in further processes (e.g. reverse osmosis) and 2) reducing the cost of the desalination process. However, input parameters such as the pressure and temperature of raw geothermal water may determine the intensity of the scaling phenomena which can exist on the surface of the nanofiltration membrane and directly impact on the efficiency of the process [10,13]. Geothermal water often exhibits high concentrations of silica, sulphates, calcium, magnesium and carbonate which can precipitate on the membrane surface and disturb the effectiveness of the process [14]. Previous research has shown that calcite, dolomite and aragonite scaling is widely encountered during the desalination of geothermal waters using membrane processes [6,14]. The degree of the scaling phenomenon observed primarily depends on the level of calcium hardness and bicarbonate alkalinity of the feed water [15–17].

There are many methods used in predicting the degree of scaling. The most popular methods are equation methods, based on the Langelier Saturation Index, Ryznar Stability Index, Pucorius Scaling Index or other measures [18]. Relative saturation indexes (%) with respect to the main salts ex.: $CaCO_3$, $CaSO_4$, $BaSO_4$, SiO2 are also calculated using related software. In most cases the use of numerical

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Table 1
Physicochemical characterisation of geothermal water tested.

Parameters	Raw geothermal water average value [mg/L]
TH[a]	584.5
Na^+	445.42
K^+	41.29
Ca^{+2}	173.86
Mg^{+2}	36.63
Sr^{+2}	5.61
Cl^-	446.70
SO_4^{-2}	723.80
HCO_3^-	287.70
H_2SiO_3	69.90
Al^{+3}	0.033
Fe^{+2}	0.140
PO_4^{-3}	0.526
Ba^{+2}	0.0172
B	8.00
EC[b] [mS/cm]	3.05
pH[c]	6.79

[a] Total hardness in mg $CaCO_3$/L.
[b] Electrical conductivity in mS/cm.
[c] pH [−].

modelling permits more accurate forecasting of the precipitation phenomena. However, it depends on the range of minerals database included in the calculation and the possibility of process parameters (pressure and temperature) being incorporated in the calculations and, also, on the physicochemical properties of the feed water.

The aim of this work is to present the results of research designed to examine the influence of selected parameters such as transmembrane pressure and the temperature of feed water on the tendency to precipitate secondary minerals during the desalination process. A calculation was done using PHREEQC, a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations [19] which is the most popular tool recommended by USGS (United States Geological Survey) and is designed to perform a wide variety of aqueous geochemical calculations. The research included all steps of analysis, from laboratory tests of selected geothermal waters, modelling research and microscopic analysis of the sediments formed on the NF membrane during the treatment processes. The purpose of the assay was to examine whether there is a reaction between process parameters (pressure, temperature) and the actual tendency to precipitate of the minerals analysed (evaluated by the variation in permeate flux).

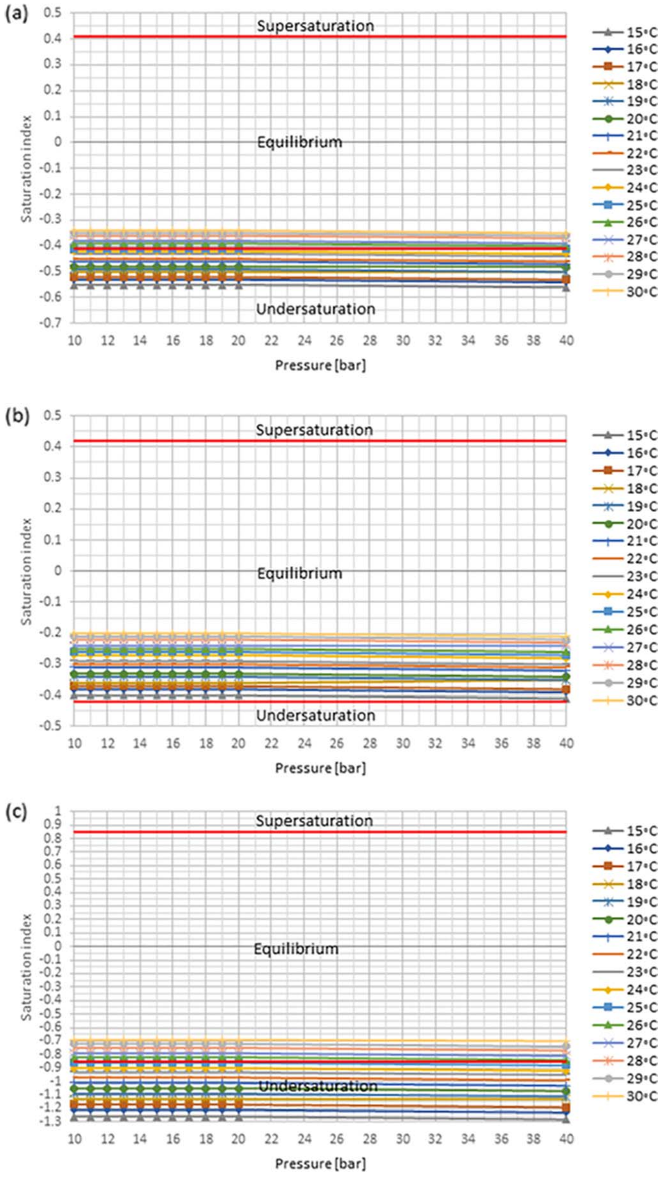

Fig. 1. The values of the Saturation Index for the (a) aragonite, (b) calcite and (c) dolomite solid phase in selected ranges of transmembrane pressure values (10–20 bar and 40 bar), including the value of water temperature (from 15 to 30 °C).

Table 2
Thermodynamic data (based on [20]).

Species	Reaction	H_r^o ± 1F (kcal/mol)	Log K_r^o ± 1F
Aragonite	$CaCO_3 = Ca^{2+} + CO_3^{2-}$ log Kr = − 171.9773 − 0.077993 T + 2903.293/T + 71.595Log_{10}T	− 2.589 ± 0.3	− 8.336 ± 0.02
Calcite	$CaCO_3 = Ca^{2+} + CO_3^{2-}$ log Kr = − 171.9065 − 0.077993 T + 2839.319/T + 71.595Log10T	− 2.297 ± 0.3	− 8.48 ± 0.02
Dolomite	$CaMg(CO_3)_2 = Ca^{2+} + Mg^{2+} + 2CO_3^{2-}$	− 11.09	− 16.54
Chalcedony	$SiO_2 + 2H_2O = H_4SiO_4$ log Kr = − 0.09 − 1032/T	4.72	− 3.55
Quartz	$SiO_2 + 2H_2O = H_4SiO_4$ log Kr = 0.41–1309/T	5.99	− 3.98
Silicagel	$SiO_2 + 2H_2O = H_4SiO_4$	4.44	− 3.018
Amorphous SiO_2	$SiO_2 + 2H_2O = H_4SiO_4$ log Kr = − 0.26 − 731/T	3.34	− 2.71

H_r^o – enthalpy of reaction; Log K_r^o – equilibrium constant for the reaction (K_r-constant reaction); kcal/mol – kilocalories per mole; 1F – the uncertainty in the listed value.