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The concentration of geothermal brines with iodine content by membrane distillation

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HIGHLIGHTS

- The application of membrane distillation for concentration of Zabłocka Thermal Brine was proposed.
- The brine was concentrated from 34 to 310gNaCl/L, and the iodine concentration up to 1gI−/L was achieved.
- The intensity of membrane scaling caused by brine during membrane distillation was studied.

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ABSTRACT

The concentration of Zabłocka Thermal Brine that contains iodine was studied in order to prepare a concentrated solution of the curative salts. The membrane distillation process was used for the concentration of brines with two kinds of polypropylene Accurel PP membranes. The solutions were concentrated from 34 to 310 g NaCl/L, and the iodine concentration increase up to 1 g I^-/L was achieved. The mineral composition of concentrated solutions, including the iodine content was determined using an ion chromatography method. The obtained rejection of solutes was close to 100%, but the small amounts of NH_3 and I_2 also diffused together with water vapor through the membrane. However, the concentration of brines using the membrane distillation process allows achieving significantly lower losses of iodine in comparison to the traditional evaporation methods. An increase in the solute concentration (to 310 g NaCl/L) caused a 30–50% drop in the yield of water evaporation through the membrane. Moreover, an intensive membrane scaling was observed, especially during the initial period of feed concentration.

1. Introduction

The curative properties of natural brines have been known and utilized by people since a long time ago for cure of many infections. Zabłocka Thermal Brine which is mining near the village Dębowiec from the depth of about 500 m, is one of more famous brines in Poland. This brine is characterized by a high iodine concentration (110–130 mg I^-/L), which is one of the highest among the brine springs so far discovered [1]. The brine also contains a significant amount of the following ions: calcium, magnesium, bromine, boron, silicon, and many other bioelements. This brine, owing to its exceptional mineral composition, is a very valuable product that can be used as a therapy for throat, larynx and bronchi problems. Moreover, it enhances the treatment of rheumatic, neurological and dermatological diseases when used for bathing.

Zabłocka Thermal Brine is not only utilized in health resorts located in the vicinity of Dębowiec village, but it can be also purchased in domestic chemist shops in the form of solutions or crystalline salt [1]. The brine for curative purposes is concentrated using a tank evaporator, until the saturated state is reached followed by the crystallization. The produced salt was called Zabłocka Curative Salt and was intensively used in healing resorts as well as at homes for bath and inhalation.

During heating of salt (NaCl) enriched with iodine (KI), the large amounts of iodine are lost from the salt along with temperature increase, especially over 400 K [2,3]. Similarly, the concentration of Zabłocka Thermal Brine by traditional evaporating methods leads to a significant loss of iodine. Decreasing the process temperature below 373 K should reduce the losses of iodine from the heating solution.

The membrane processes can be the alternative methods used for the concentration of brines. One of the possibilities is the membrane distillation (MD), which is usually carried out below 363 K [4–7]. In this process, a hydrophobic porous membrane separates the concentrated solution from obtained distillate. The membrane pores can be only filled by the gas phase; therefore, the solutions separated in MD cannot cause the wettability of used membranes [7,8]. Due to the discontinuity of the liquid phase across the membrane, the

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water flux in MD is not affected by the osmotic pressure gradient across the membrane, and the concentrated salt solutions, close to the saturation state, can be obtained in this process [9,10].

The solution concentrated in the MD process is heated below the boiling point, and the volatile components are evaporated from the feed/membrane interface. Subsequently, the formed vapor diffuses through a gas layer in the membrane pores on the other side, where it undergoes the condensation in the cold stream of distillate. The driving force for the mass transport is a gradient of vapor pressure, which results from the differences in both the temperatures and compositions of solutions in the layers adjacent to the membrane [4–9]. The MD separation mechanism is based on the vapor/liquid equilibrium of a liquid mixture, therefore, the permeate composition is dependent on the partial pressure of respective components of the feed. For the solutions containing non-volatile solutes only water vapor is transferred through the membrane; hence, the obtained distillate comprises demineralized water [7–11]. When a feed contains various volatile components, they are also transferred through the membranes to the distillate [8,12]. However, the feed has definitely lower temperature than that of liquid boiling in the evaporators. This should significantly limit the influence of temperature on the iodine loss.

Rich mineral content of the natural brines may result in the formation of deposit on the membrane surface (scaling) during the MD. The scaling phenomenon is one of the main reasons, which hinders the application of the MD process [10–14]. For this reason one should restrict the possibility of occurrence of the oversaturated state of dissolved components in the feed during the concentration of solutions [9–11]. In the case of the concentration of brines, it can be achieved by the connection of MD installation with salt crystallizer [9,15,16]. The other possibility creates the accelerated precipitation softening (APS), which was integrated with direct contact membrane distillation (DCMD) to establish a desalination process for high-recovery desalting of reverse osmosis (RO) concentrate [11].

The effect of scaling can be limited in the same cases by a periodical cleaning of the membranes [14,17]. During the separation of RO brines by MD the silica and calcium sulphates exceeded their saturation and were precipitated on the surface of polypropylene (PP) and PTFE membranes [14]. The membranes were cleaned with disodium ethylenediaminetetraacetic acid (Na_2EDTA). In contrast to the membranes made of PTFE, the performance of PP membranes was similar before and after cleaning. This implies that a scale deposition on the PP membranes is less strongly adhered to the membrane surface and can be removed using a simple cleaning method. Moreover, the results reported in this work suggest that membrane scaling caused by $CaSO_4$ can be effectively controlled by the removal of the nucleation sites from the membrane surface using the water for the module rinsing in a period shorter than the induction time for the growth of $CaSO_4$ crystals [10].

The mineral composition of Zabłocka Thermal Brine [1] indicates that the precipitation and/or crystallization of sparingly soluble salts on the membrane surfaces can occur during the concentration of this brine by the MD process, which decreases the durability of membranes. The possibility of scaling occurrence and its influence on the course of the MD process of Zabłocka Thermal Brine was studied in this work.

2. Theory

The iodine forms the ions with the different oxidation states, which range from −1 to +7 in the aqueous solutions. The majority of metal-iodides are soluble and will be readily dissolved in water to form iodide ions. Usually, when the studies are carried out, the concentration of iodide (I^-) and iodate (IO_3^-) ions is most often analyzed, because these are the two major forms of their occurrence [18]. Although they are non-volatile, but under the appropriate conditions, they can undergo the transformation to the species I_2, which are sparingly water-soluble and possess volatile properties. The stability of a given form of iodine depends to a large degree on the pH of the aqueous environment. In a neutral and alkaline environment iodine forms the iodide ion and HOI acid:

$$I_2 + OH^- \Leftrightarrow I^- + HOI. \tag{1}$$

The acid molecules undergo a further transformation to the ions IO_3^- and I^-:

$$3HOI \Leftrightarrow 2I^- + IO_3^- + 3H^+ \tag{2}$$

which can be described in summary by the following equation:

$$3I_2 + 3H_2O \Leftrightarrow 5I^- + IO_3^- + 6H^+. \tag{3}$$

In the acid environmental (≤pH 4) at the appropriate concentration of iodide is formed I_2. In the pH range from 5 to 10 the volatile iodine species I_2 is in the equilibrium with the iodide ions I^- forming a complex I_3^- (np. $KI_3 * H_2O$) [12]:

$$I_2 + I^- \Leftrightarrow I_3^-. \tag{4}$$

On the other hand, in the strongly alkaline solutions (pH > 10), the HOI dissociates with the formation of the OI^- ions:

$$HOI \Leftrightarrow H^+ + OI^-. \tag{5}$$

With the access of air or ozone, the oxidation reaction catalyzed by the metal ions such as Fe^{2+} can also proceed in a solution:

$$2I^- + 1/2O_2 + H_2O \Leftrightarrow I_2 + 2OH^-. \tag{6}$$

The hydrolysis reaction (3) strongly depends on the temperature and the content of I_2 decreases by about 100 times, when the solution temperature will be increased from 298 to 373 K [3]. For this reason, the concentration of brines with iodine in the evaporators leads to the iodine losses. Moreover, the iodine forms an aerosol during the water evaporation, which additionally increases its losses during the concentration by the evaporation method. A phenomenon of droplet entrainment does not occur in the MD process, therefore, this process was utilized in this study for the concentration of Zabłocka Thermal Brine.

3. Experimental

The studies on the brine concentration were carried out using a variant of direct contact MD (DCMD). The MD installation, presented previously [17], consisted of two thermostatic cycles (feed and distillate) that were connected to a capillary membrane module. Two types of membrane modules made of polypropylene membranes, capillary Accurel PP Q3/2 and tubular Accurel PP V8/2 HF (Membrana GmbH, Germany) were used. The applied membranes had the pore sizes with the nominal diameter of 0.2 μm, and the porosity of 73% (the manufacturer's data). The outside/inside diameters of Q3/2 and V8/2 HF membranes were equal to 1/0.6 mm and 8.6/5.5 mm, respectively. In the module MK1 (shell diameter 2.1 cm), the three membranes V8/2 HF were assembled with a length of 17 cm, whereas the module MK2 (shell diameter 1.35 cm) was made of 75 membranes Q3/2 with a length of 24 cm each.

The Zabłocka Thermal Brine obtained from Dębowiec Mine and Saltworks (Poland) was used as a feed in the presented MD study. This brine was subjected to iron removal and filtered after the extraction