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Rejection of nuclides and silicon from boron-containing radioactive waste water using reverse osmosis

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ABSTRACT

Reverse osmosis has been successfully utilized for waste separation across various fields. In this work, RO membrane was investigated for the separation of weakly electrolytic silica and boron, which was meaningful for potential boron reuse and waste reduction during treatment of low level radioactive waste water. The influences of temperature, pressure, and pH were tested. As the recovery rate rose to 80%, the flux decreased and the permeate concentration increased slightly. A higher temperature of 55 °C led to a higher silica and boron separation efficiency without a large loss in nuclides rejection. Under these conditions the recovery of boron is 46.58%, and the decontamination factors (DF) of silicon, Cs, Sr, and Co are 29.3, 4.54, 58.88, and 70.41, respectively. Assuming reasonable system design, the recovered water containing a high concentration of boron and a low concentration of silica is acceptable for reuse.

1. Introduction

Membrane technology has been widely used in seawater desalination [1,2], waste water treatment [3], and water purification [4]. The applicability of membrane separation processes for treatment of hazardous and complex aqueous industrial waste is well known. In recent years, many researchers have attempted to employ reverse osmosis (RO) in order to remove strong electrolytic nuclides such as cesium, strontium, and cobalt during the treatment of low level radioactive wastewaters (LLRWs) [5,6]. Using this method, these trace nuclides can efficiently be removed even though background components such as boron and various salts exist in concentrations several orders of magnitude higher than the nuclides [7]. During such treatment cesium rejection is higher than 90%, and both strontium and cobalt rejection ranges from 95% to, in some cases, 99.5% [8–10].

As described above, under normal circumstances reverse osmosis has an extremely high level of rejection for strong electrolytic solutes at high concentrations. However, in the case of weak electrolytes such as boron or silica, rejection rates by reverse osmosis have significant differences. Researchers have shown that the rejection of boron is only about 40–60% under neutral conditions [7,11]. Meanwhile, the rejection of silica has been measured to be about 97–99% [12]. Due to changes in the dissociation ratio, the rejection rates of weak electrolytes are likely to be heavily influenced by operating conditions [13]. For instance, an increase in pH would promote the dissociation of silica and boron and result in an increase in rejection [14]. In addition, the temperature, cross-flow rate, and pressure also affect rejection of weak electrolytes [15,16].

The differences in rejection rates between different electrolytic components offer possibilities for good separation. These differences are especially important for the treatment of LLRWs from Nuclear Power Plants, which must be purified before discharge into the environment and contain both large amounts of boron (average concentration of 500 mg L^{-1}) and low levels of radioactive nuclides. Traditional technology such as ion-exchange would produce a large volume of radioactive waste, and use of evaporation consumes large amounts of energy and is limited in concentration ability due to boron crystallization (about 15,500 mg L^{-1}) [17]. In order to minimize the final volume of radioactive waste, a promising solution would be to recover boron from LLRWs and reuse it in the primary coolant system of the nuclear power plants. To achieve this reuse plan the radioactive nuclides, strong electrolytic components, and weak electrolytic components such as Si, must be separated from the recovery water. Due to the obvious rejection differences, a RO unit can give a favorable separation of trace nuclides and strong electrolytic components from the boron containing LLRWs [7]. Particular attention must be paid to the possibility of silica separation from LLRWs containing excess boron.

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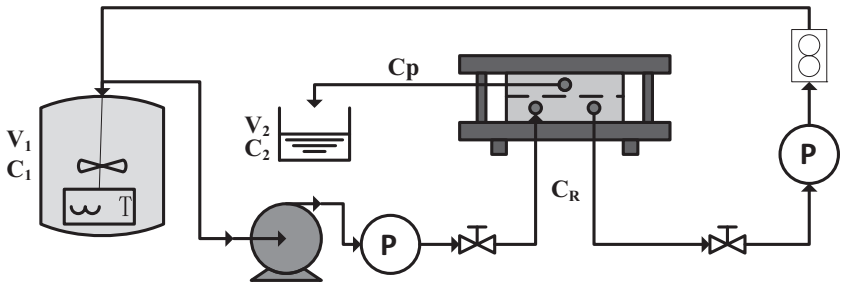

Fig. 1. Scheme of the RO set-up.

Previous and similar research was conducted by Liang et al. In their work, researchers used two membranes to reduce silica concentration from 3.15 mg L^{-1} in the original solution to 0.605 mg L^{-1}, with a small amount of boron waste with the concentration of 2.52% [18,19]. The successful separation process is based on the different rejection rates of silica (usually higher than 95%) versus boron (usually only 40–80%) [20]. As opposed to Liang's study, this work focuses on selecting optimized conditions for the separation of boron from silica containing LLRWs, as well as the different types of fouling that occur when using an LE membrane. This membrane has the advantage of high nuclides rejection and low boron rejection, as shown in our pervious study [7]. The influence of temperature, pressure, and pH on the rejection of typical nuclides (cesium, strontium, and cobalt) as well as silicon in boron-containing water was investigated. The results herein provide an improved understanding of a boron reuse system design for PWRs (Pressurized Water Reactor) as well as expanded applications for RO technology in nuclear industry.

2. Experiment

2.1. Materials and Installation

Experiments were carried out in laboratory-scale installations, shown schematically in Fig. 1. Raw water was initially pumped into an intermediate buffer vessel equipped with a temperature control system. It was then conducted across a cross-flow membrane-filtration apparatus (SEPA CF II) equipped with a flat sheet membrane and using a controlled feed flow of 0.4 m s^{-1}. The membrane-filtration apparatus was manufactured by GE Corp and had a flow channel measuring 146 mm × 96 mm × 0.86 mm and an effective membrane area of 140 cm^2. At the beginning of each experiment, a stabilized flux was achieved through membrane sample compaction using demineralized water at 0.4 MPa for 6 h.

7.5 L of raw water containing 500 mg L^{-1} boron, 8 mg L^{-1} silica, 500 mg L^{-1} Cs, 500 mg L^{-1} Sr, and 500 mg L^{-1} Co. The concentrate was conducted back to raw water (V_1), while the permeate was collected separately (V_2) in order to achieve a high recovery rate (80%) Concentrate and permeate samples were measured intermittently with the rising recovery rate. Various operating conditions were tested including temperature (15, 25, 35, 45, and 55 °C at a pressure of 1.4 MPa and original pH), pressure (1.2, 1.4, and 1.6 MPa at 25 °C and original pH) and pH (6, 8, and 9.5 at 25 °C and a pressure of 1.4 MPa). For each experiment, operation time and permeate flux were also recorded. After a recovery rate of 80% had been achieved, each membrane was quickly flushed for about 5 min using demineralized water and then dried by vacuum.

Experiments were carried out using commercially available reverse osmosis membrane (LE membrane, provided by Dow Chemistry). Its properties as given by the manufacturers are listed in Table 1.

Table 1
Characteristics of RO membrane materials.

Membrane	Material	Surface charge	Specific flux (L m^{-2} h^{-1})	R_{stable} (%)	R_{min} (%)
LE	Polyamide	Negative	49.55	99.30	99.00

2000 ppm NaCl, 10.3 Bar, 25 °C, 15% recovery, pH = 8; *c*: 500 ppm NaCl, 6.9 Bar, 25 °C, 15% recovery, pH = 8. R_{stable} means the average rejection and R_{min} means the minimized rejection.

2.2. Chemicals and raw water

Demineralized water containing $CsNO_3$, $Sr(NO_3)_2$, or $Co(NO_3)\cdot 6H_2O$ bearing solutions were used for experiments, with final Cs (I), Sr(II), and Co(II) concentrations equaling around 500 μg L^{-1} each. A boron concentration of 500 mg L^{-1} was achieved by adding boric acid. Sodium metasilicate nonahydrate ($Na_2SiO_3\cdot 9H_2O$) was added to achieve a silicon concentration of 8 mg L^{-1}. The pH of the raw water was adjusted using NaOH solution. All chemicals used were analytical grade.

2.3. Analytical methods

The concentrations of Cs, Sr, and Co were analyzed using a Thermo ICP–MS XII based on the general rules for inductively coupled plasma-atomic emission spectrometry (JY/T 015-1996). Silicon was analyzed using an ICP spectrometer (Icap 7000 SERIES). Boron was analyzed using a SHIMADZU UV-1800 spectrophotometer based on the Methylene amine-H acid spectrophotometric method. Fouled membrane surface imaging was performed using Scanning Electron Microscopy (SEM, HITACHI S-5500).

2.4. Assessment methods

Permeate flux (J) (L m^{-2} h^{-1}) was calculated using formula (1):

$$J = \frac{m}{\rho \cdot A \cdot t} \quad (1)$$

where t and m are time and permeate mass, respectively; ρ is the density of raw water; and A is the membrane area.

Rejection (R_j) was calculated using formula (2), where C_p and C_R are the concentrations (μg L^{-1}) of solutes in the permeate and the concentrate at an equal recovery rate.

$$R_j = \frac{C_R - C_P}{C_R} \times 100\% \quad (2)$$

Recovery rate (R_R) and Concentration factor (CF) were calculate using formulas (3) and (4), where V_2 is the permeate water volume, V_0 is the initial raw water volume, C_1 is the concentration of solutes in the concentrate water, and C_0 is the initial concentration of solutes in the raw water.