Preliminary study on recovering lithium chloride from lithium-containing waters by nanofiltration

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Abstract

Process assessment experiment was carried out to investigate the applicability of nanofiltration (NF) for recovering lithium chloride from lithium-containing waters. A Desal-5 DL membrane element was adopted to treat diluted bittern containing lithium chloride and large concentrations of magnesium, boron and sulfate. The mass transfer and separating mechanism of the process were discussed qualitatively. It was suggested that ionic fractionations were governed by the combination of Donnan exclusion, dielectric exclusion and steric hindrance. At higher concentrations, steric hindrance became remarkable due to the formation of ion pairs, ion clusters and molecules. Experimental results showed that the DL membrane exhibited satisfactory rejection of sulfate and moderate rejection of magnesium but poor rejection of boron. For recovering lithium, DL performed economically poorly compared to electrodialysis.
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1. Introduction

Nanofiltration (NF), as a pressure-driven separation process that forms the transition between ultrafiltration (UF) and reverse osmosis (RO), is undergoing fast developments in recent years. Compared to RO, NF has lower energy consumption and higher fluxes, which enables its versatility in industrial and environmental applications. NF is deployed either solely or integratedly coupled with UF, RO, ED and other separation processes to solve many specific technical problems [1,2]. In particular, NF is repeatedly reported as a highly effective method for the extraction of monovalent ions from systems containing multivalent ions.

Lithium, as the lightest metal element, is widely used in various fields such as lithium electrolytes for secondary batteries, lithium additives for functional materials, lithium-based lubricating greases and medical additives. Its application and consumption is steadily growing in recent years. The recovery of lithium from nature, lithium-containing waters in particular, is a demanding task for many years. Lithium is naturally coex-

isting with many other minerals such as magnesium and boron and takes only a small proportion in most of its deposits, which makes its extraction an extremely challenging job.

The purpose of the present work was to investigate the applicability of nanofiltration in recovering lithium chloride from multicomponent systems such as lithium-containing saline waters, especially brines containing dominant quantities of divalent and multivalent ions, based on process assessment experiments and technical comparison.

2. Materials and methods

2.1. Experimental set-up

Fig. 1 depicts the experimental set-up characterizing of a two-step filtration of the concentrated brine before dilution. When operated in a batch-wise circulating mode, the feeding temperature was quickly ascending. So a heat exchanger was added before the membrane element. Between the feed pump and the high-pressure pump, a polypropylene microfilter was connected to ensure the feed was manipulated at a turbidity of less than 1.0 NTU. The permeate solution was collected in the permeate tank for sampling and analysis. The NF element was a spiral

Nomenclature

i, j	component i, j
R	rejection ratio
V_P	accumulated permeate volume (L)
V_F	feed volume (L)
C_P	permeate concentration ($g\,L^{-1}$)
C_F	feed concentration ($g\,L^{-1}$)
S	permselectivity
π	osmotic pressure (MPa)
N	flux of component across membrane ($g\,m^{-2}\,h^{-1}$)
N_P	flux of permeate across membrane ($L\,m^{-2}\,h^{-1}$)
Δp	operating pressure (MPa)
P'	specific energy consumption ($kwh\,(g\,Li)^{-1}$)

wound Desal-5 DL 2540C model supplied by GE Osmonics, which is of a polyamide composite type having an active area of $1.77\,m^2$.

2.2. Preparation of feed

The feed was obtained by diluting a concentrated brine solution (bittern) with soft water. The bittern was obtained from solar ponds of Qinghai Lithium Limited Company, which is situated at the East Taijinaier Salt Lake. The bittern characterizes with a TDS over $500,000\,mg\,L^{-1}$, substantially free of sodium and potassium ions and having a pH of 4.7. At this high concentration, the bittern is not suitable for the feed of NF separations. Therefore, dilution is necessary. Before dilution, the bittern was sequentially passed through one multimedia filter and one manganese dioxide sand filter to bear a turbidity of less than 1 NTU and ferrous and manganese content of less than $0.1\,mg\,L^{-1}$, respectively. After dilution, the composition characteristics of the feed were analyzed, and calculated by PHRQPITZ V1.12, as shown in Table 1.

2.3. Operating conditions

The NF system was operated at a feeding pressure of 161 psig (1.10 MPa) with an average head loss of 2.0 psig (13.8 kPa) corresponding to a crossflow rate of $120\,L\,h^{-1}$ on the concentrate side. During the separation process, the concentrate temperature was monitored, and manipulated below $40\,^\circ C$ by adjusting the flow of the heat exchanger.

2.4. Measurement methods

The methods and instruments are briefly described in Table 2.

3. Results and discussion

The overall process performance includes both technical and economical aspects, which are primarily dependent on the rejection and permeation characteristics of the solute ions, as well as the specific raw material (water) consumption. Thus, to recover lithium chloride effectively and economically requires the NF membrane has high rejections of magnesium, sulfate and boron, but low rejections of lithium and chloride, as well as enough high permeate fluxes. In [3], an economic assessment model was presented with the conclusion that system cost can be significantly reduced by adopting a looser NF membrane. Therefore, the membrane in consideration should be both adequately selective for monovalent ions and loose enough to be more permeable. The Desal 5DK and Desal 5 DL membranes are suitable for rejecting multivalent ions but permeating monovalent ions. However, the latter has larger pore sizes [4] and exhibits higher fluxes. For economical considerations, we adopted Desal 5 DL for the NF assessment.

3.1. Rejection performance and separation mechanism

The prevailing conception of NF separation in nowadays is mass transport inside NF membranes is governed by the
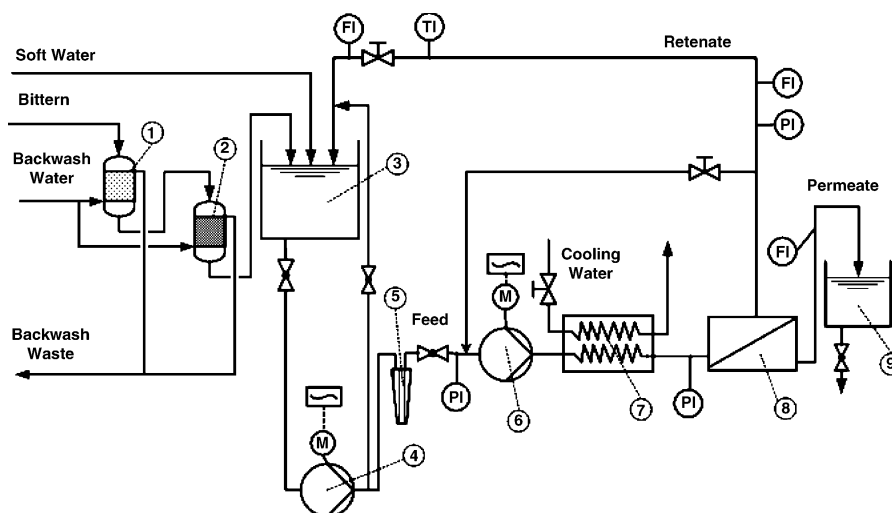

Fig. 1. Experimental set-up of the NF treatment; (1) multimedia filter; (2) manganese dioxide sand filter; (3) feed tank; (4) feed pump; (5) polypropylene microfilter; (6) high-pressure pump; (7) heat exchanger; (8) NF membrane element; (9) permeate tank.