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Influence of speciation during membrane treatment of uranium contaminated water

Michael Hoyer [a,*], Denise Zabelt [a], Robin Steudtner [b], Vinzenz Brendler [b], Roland Haseneder [a], Jens-Uwe Repke [a]

[a] TU Bergakademie Freiberg, Institute of Thermal, Environmental and Natural Products Process Engineering, 09596 Freiberg, Germany
[b] Helmholtz-Zentrum Dresden-Rossendorf e.V., Institute of Resource Ecology, 01314 Dresden, Germany

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ABSTRACT

Membrane treatment can be used to selectively remove chemical species, such as uranium complexes from mine effluent. However, uranium speciation depends on different chemical factors such as inorganic and organic reaction partners, temperature, and pH, complicating a deeper understanding of the underlying mechanisms. Currently, membrane separation is not employed in the treatment of uranium-bearing effluent from the former uranium mines in Germany. In this study the potential of membrane separation for selective uranium removal was assessed for two real water samples. Speciation for such complex chemical conditions was determined with two independent methods in parallel: predictive modeling using the speciation codes “PhreeqC” and “EQ3/6”, and direct measurement using cryo-TRLFS (time-resolved laser-induced fluorescence spectroscopy). Different nanofiltration membranes and reverse osmosis membranes were characterized in a first step, for their potential rejection, and pure water flux. The best performing membrane was then employed in cross-flow experiments and reached retentions over 99% and U/Na-selectivities of 200. Uranium retentions showed a low dependency on feed uranium speciation. Continuing research is necessary for an exact determination of separation mechanisms for each membrane.

1. Introduction

In 1990, when uranium production was abandoned in the eastern part of the now reunited Germany, the legacy left behind was a heavy burden of environmental damage but also a potential future hazard [1]. The Wismut GmbH was established as a federal company, in charge of the environmental cleanup. As part of the remediation program five underground mines were flooded, generating contaminated water to be treated over the long-term. Different in situ methods were introduced, such as immobilization (where saturated barite solution is injected in order to immobilize contaminants), the reactive barrier approach (zero-valent iron addition, to establish reducing conditions), and also changes in the mine water management scheme, such as plugging the mine. Despite the success of these measures the effluent that leaves some abandoned mines needs to be further treated using methods such as aeration or precipitation. Currently, membrane treatment is not in use for uranium removal there, despite the high potential shown in other studies on membrane treatment of acid mine drainage [2]. Uranium concentrations in the effluent can reach up to 10 mg/l, well above the current limit for discharge of 500 μg/l [3].

Membrane treatment of uranium contaminated water has been subject to numerous studies in contexts such as treatment of drinking water or effluent from uranium conversion processes. In all studies involving reverse osmosis (RO) and nanofiltration (NF), membrane filtration proved to be a promising technology for uranium removal. This high potential has already been shown in 1976 by Sastri [4] using cellulose acetate membranes for the treatment of uranyl sulfate solutions with very high uranium concentrations of up to 5 g/l, nevertheless achieving retentions in the range of 91% to 99.8%.

Notwithstanding such high rejections, a fundamental understanding of the underlying separation processes is the key to a systematic optimization of rejection and selectivity. Unfortunately, early studies lacked such an understanding as they observed anomalous phenomena, not in agreement with the standard models of membrane filtration. The following examples illustrate the anomalous phenomena. According to standard models, higher concentration increases salt flux thereby decreasing retention. For

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Abbreviation: cryo-TRLFS, time resolved laser-fluorescence spectroscopy at low temperature.

* Corresponding author. Tel.: +49 15223172877.
E-mail address: Michael.Hoyer@tun.tu-freiberg.de (M. Hoyer).

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uranium contaminated waters, the reverse correlation has been observed repeatedly and consistently for cellulose acetate RO membranes [4,5]. Besides this unexpected positive correlation between uranium feed concentration and retention the effect of pH was in disagreement with the expectations, too. In a study using a polyamide RO membrane by Chen in 1992 [6] uranium rejections were consistently highest at the lowest pH in this study (2.8) with rejection values reported as 100%. At all other pH values in that study no obvious correlation between uranium rejection and pH exists. Thus, this sudden, strong pH dependence is surprising, and has not been clarified by the authors.

In 1992, Prabhakar [5] suggested that phenomena like the positive correlation between uranium concentration and retention could be attributed to the influence of uranium speciation, taking a first step towards a deeper understanding of the processes. However, due to the complex water composition verification of this hypothesis is difficult and the authors could not proceed beyond speculation. To avoid this complication, in 1999 Raff [7] used membrane separation for an aqueous uranyl carbonate system with known speciation and was thus able to document that a speciation-effect for membrane filtration of uranium contaminated water exists. The results from five different NF flat sheet membranes showed that rejection was highest for negatively charged species and lower for neutral and positive species, making charge effects primary suspect for the separation mechanism.

In 2008, evaluation of species-membrane interactions for complex systems was approached by Favre-Réguillon et al. [8] using four different NF flat sheet membranes. The speciation was calculated according to thermodynamic equilibria conditions for the given solution composition using an appropriate database and the speciation code "Chess". The study highlighted that the influence of membrane properties on retention dominates the influence of uranium speciation, pressure, feed concentration, and cross-flow velocity. The tested membranes were in the range of 20%, 90%, and close to 100% uranium retention, respectively. Though there was considerable progress in the past towards a more mechanistic description of mass transport in nanofiltration membranes the influence of speciation remains complicated because species can transform between each other and it is not even clear if the species in the bulk phase remain stable in the membrane phase.

In this study two complex mine water samples were treated with different commercial NF and RO membranes with the objective to selectively remove uranium. Speciation was influenced by variation of pH, concentration, and available ligands. To assess the effect of speciation for such complex chemical conditions, two methods for speciation analysis were used in parallel: calculation using chemical speciation codes, such as PhreeqC [9], and direct measurements using time resolved laser-fluorescence spectroscopy at low temperature (cryo-TRLFS at 153 K) [10]. The potential applicability of membrane filtration as a uranium selective separation process was then evaluated.

In solution a chemical element exists in certain different forms which are called species, e.g. as a (sometimes large) complex or as a free ion [11]. The speciation of the solution is the percent distribution of a chemical element among its different species. Since the speciation determines the most important feed characteristics, charge, size, mobility, and sorption behavior, it needs to be considered to evaluate the performance of membrane separation processes.

2. Experimental

2.1. Membrane filtration facilities

Experiments were carried out with two different lab facilities. Membrane characterization and screening was performed with a stirred batch cell. This cylindrical stainless steel cell is pressurized with nitrogen from a gas cylinder using a pressure transducer and a manometer to manually adjust the pressure. The solution is pressed through the membrane which is supported by a sinter metal plate at the bottom of the cell. The effective membrane area of the stirred dead-end unit is about 40 cm^2. To increase convective transport within the feed solution a magnetic stirrer was used rotating at 500 min^{-1}. All batch experiments were performed at ambient temperature. The piping and instrumentation diagram (P&ID) of the batch facility is shown in Fig. 1.

The dilution, pH change, and long-termed experiments were done with the cross-flow membrane unit. The rectangular stainless steel channel is pressurized using a high pressure plunger pump (Catpumps model 1051D) with the trans-membrane pressure being controlled using a control valve and the commercial software LabVIEW [12]. The pump's flow rate is adjusted to meet the set point cross-flow velocity also using process control with LabVIEW and a flow meter (Bürkert SE30). The effective membrane area of the cross-flow test cell is about 80 cm^2. Fig. 2 visualizes the design of the cross-flow test cell. A detailed description of the test cell is given in [13].

2.2. Water samples used as feed solutions

In Germany huge efforts have been put in the remediation of former uranium mining sites. Effluent from two such former uranium mining sites was supplied by the Wismut GmbH as feed solution for this study. The elemental composition of the two solutions named 1 and 2, as analyzed by ICP-MS (refer to Section 2.4) is displayed in Table 1. The results from TRLFS as well as from the speciation modeling showed that the samples have a distinctly different composition, with sample 1 clearly being dominated by sulfate anions and sample 2 by a high carbonate concentration, which can be related to its pH of 7.8 where carbonate is more stable. However, this original carbonate content in sample 2 corresponds to a partial pressure of $10^{-2.3}$ bar, well above the content in ambient air. Thus, a steady out-gassing of this sample was observed, accompanied by an increase in pH up to final values of 8.1. Accordingly, all speciation models for sample 2 adjusted the real carbonate content to the value in air, i.e. $10^{-3.5}$ bar.

2.3. Speciation modeling

One method to determine the theoretical uranium speciation for waters of complex composition is by means of speciation modeling. There, thermodynamic data such as complex formation constants and solubility-products are required; in case of high ionic

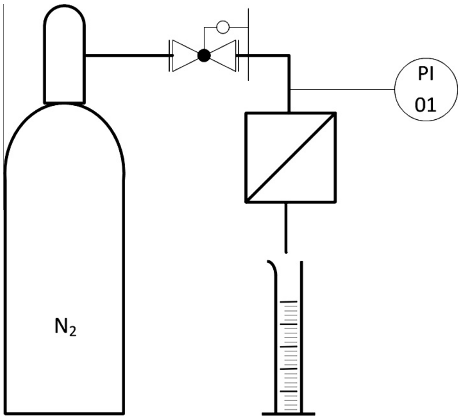

Fig. 1. P&ID of the stirred dead-end unit. Stirring bar inside the cell not symbolized.