

## Nanofiltration – A new separation pathway in secondary mining

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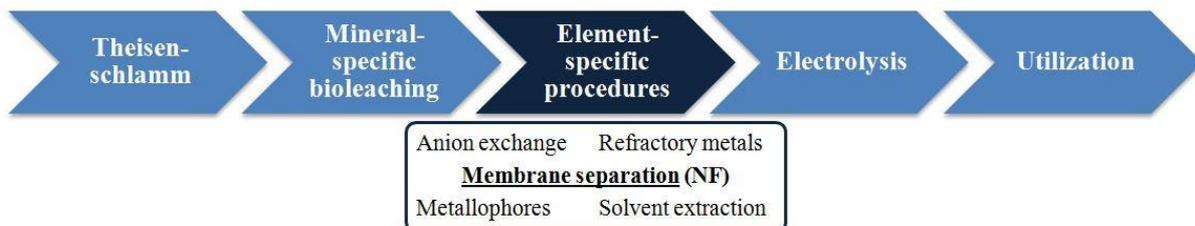
### Abstract

Since decades, the demand of strategic elements is increasing. On the one hand, the industrialization of emerging countries is advancing due to the desire of a higher standard of living. On the other hand, the technical progress of the industrial countries leads to an enhanced provisioning of raw materials, such as strategic elements. Therefore, the supply is becoming increasingly difficult and supply bottlenecks might occur. Hence, the potential of secondary mining has to be exploited to uncover yet untapped resources. In the present study, the potential of a Theisenschlamm mono-landfill, a residue of German copper smelting with various strategic elements (e.g. Co, Ge, Mo, Re, Sb) included, shall be illustrated. By means of a hybrid process, consisting out of bioleaching and downstream processing, the target elements shall be mobilized and processed. As part of the element-specific procedures, the presented study investigates the applicability of nanofiltration to separate mono- and divalent metal ions in aqueous solution. Three thin-film polymeric nanofiltration membranes were investigated to determine the pH-dependent separation performance of Ge, Mo, and Re. Membrane screening experiments were conducted in dead-end set-up (15 bar, 25 °C) with the single and combined elements and aimed at identifying a suitable membrane for the proposed cross-flow set-up. The results demonstrate that rhenium could be separated from the multicomponent solution by the utilized RO90 membrane, which accounts for a market potential of approx. 19 Mio. \$.

Key words: Secondary mining, Theisenschlamm, strategic elements, bioleaching, nanofiltration

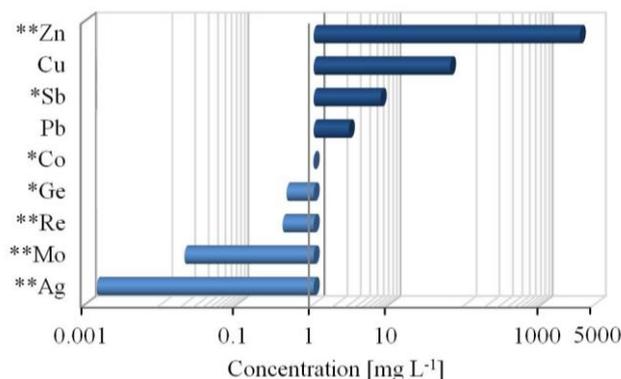
### Introduction

The investigated mining residual, the so-called Theisenschlamm, is a fine-grained flue dust with a mean particle diameter of 1.55 µm. It remained from top gas scrubbing during copper shale smelting in a blast furnace. Approximately 220,000 t of this by-product were deposited between 1978 and 1990 in Saxony-Anhalt in Germany (Weiss et al. 1997; Lorenz et al. 1992; Lorenz 1994). Besides the main components zinc and lead, various critical and candidate critical raw materials (European Commission 2014) are included from very small but right up to very significant amounts (see Figure 5A). Pyrometallurgical and hydrometallurgical attempts were applied to extract valuable components from the Theisenschlamm matrix, but until today a suitable process is missing (Weiss et al. 1997; Lorenz et al. 1992; Leipner et al. 1991). With beginning of 2015, the interdisciplinary r<sup>4</sup>-joint research project was commissioned to develop an energy-efficient, economical, and eco-friendly process to extract and process the target elements from the Theisenschlamm (see Figure 1).



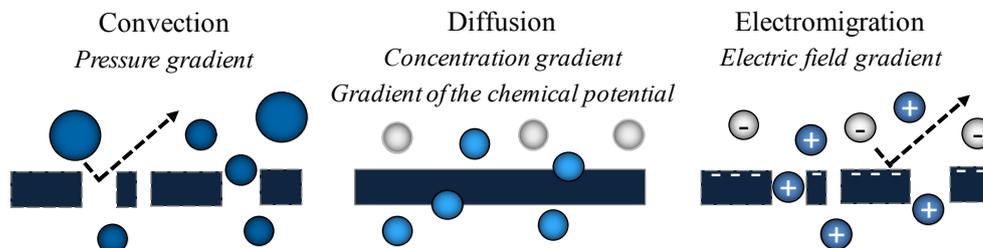
**Figure 1** Proposed process chain of the r<sup>4</sup>-joint research project to extract, separate, and concentrate the target strategic elements from the Theisenschlamm matrix by bioleaching and downstream processing.

As shown in Figure 1, a variety of element-specific procedures like nanofiltration (NF) shall be conducted to separate and concentrate the strategic elements from the obtained multicomponent leaching solution. By bioleaching even low-grade sulfidic mining residuals can be solubilized. Acidophilic microorganisms like *Thiobacillus* and *Acidithiobacillus* are able to oxidize sulfides, sulfur and iron(II) and mobilize sulphate, iron(III), and other soluble metal compounds (Bosecker 1997; Das et al. 1999). Initial bioleaching experiments were performed in a 2 L stirred-tank bioreactor with *A. ferrooxidans*, a 9K<sub>25</sub>-medium, and 4 % (w/v) Theisenschlamm. The leaching solution was analyzed with ICP-AES (Zn, Cu, Sb, Pb, Mo) and ICP-MS (Co, Ge, Re, Ag). An excerpt from the analysis is shown in Figure 2 (Klink et al. 2016).



**Figure 2** The chemical composition of the bioleaching solution of Theisenschlamm (Klink et al. 2016); \*critical, \*\*candidate critical raw material (European Commission 2014).

Figure 2 illustrates that the bonded metals can be solubilized from the Theisenschlamm matrix by bioleaching, but the concentration of the extracted elements is strongly varying (Klink et al. 2016). As a new environment-friendly pathway in secondary mining, the nanofiltration enables a selective separation and concentration of dissolved metals in aqueous solution. Based on adsorption and convective (size exclusion), diffusive, and electromigrative (charge interaction) transport mechanisms (see Figure 3), the retention of dissolved components is influenced. It is possible that the different retention mechanisms exist alongside and affect each other (Mulder 1996; Shen and Schäfer 2014).



**Figure 3** Simplified retention mechanisms and related driving forces of the nanofiltration according to Shen and Schäfer (2014).

For years, the membrane technology is used for water and wastewater treatments and synthetic nanofiltration membranes are in focus due to their high selectivity towards mono- and multivalent ions, wide pH range, and high permeability (Mulder 1996). The presented study investigates the pH-dependent separation performance of three polyamide nanofiltration membranes towards Ge, Mo, and Re in dead-end set-up. The aim is to examine occurring retention mechanisms and to identify a suitable membrane for processing the multicomponent leaching solution in the planned cross-flow set-up.

## Materials and methods

### Analytical investigation of Theisenschlamm

Theisenschlamm was sampled from the mono-landfill in Helbra (Saxony-Anhalt, Germany) at a depth of 4 m in May 2015. The total element concentration of Cu, Mo, Pb, Sn, Sb, and Zn was analyzed by energy dispersive X-ray fluorescence spectrometry (EDXRF; SPECTRO XEPOS HE, X-Lab Pro 5.1

Software). The trace elements Ag, Co, Ge, and Re were analyzed in an *aqua regia* extract of the Theisenschlamm using ICP-MS (Agilent 7700) due to the limitation in determination of EDXRF.

### *Synthetic feed solutions*

On the basis of the bioleached Theisenschlamm (see Figure 2), synthetic feed solutions were prepared, which contained  $1 \text{ mg L}^{-1}$  Ge ( $\text{GeO}_2$ , 99.999 %, metals basis),  $0.5 \text{ mg L}^{-1}$  Mo ( $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ , 98 %), and  $1 \text{ mg L}^{-1}$  Re ( $\text{NaReO}_4$ , 99+%, metals basis, Re 68 %), either as single element or in combination. The aim was to investigate the pH-dependent retention mechanisms with and without mutual interferences. Due to the fact that bioleaching is carried out between pH 1.5 – 3 (Bosecker 1997), experiments were conducted at pH 2 and 4. Moreover, pH 7 was examined to investigate the influence of varying ionic species and changing membrane surface charge. The requested pH was adjusted with 0.1 M NaOH and 0.1 M  $\text{H}_2\text{SO}_4$ . The feed concentration was verified with ICP-MS (Agilent 7700). In advance, the samples had to be acidified with  $20 \mu\text{L HNO}_3$ .

### *Polymeric nanofiltration membranes*

Three nanofiltration membranes from the Alfa Laval Corporate AB (Lund/Sweden) were investigated to examine the retention mechanisms of Ge, Mo, and Re in dependence of pH. A summary of the membrane characteristics is given in Table 1.

**Table 1** Characteristics of the utilized polymeric nanofiltration membranes. Unmarked information has been provided by the manufacturer.

Membrane	NF (NF99, NFT-50)		NF99HF		RO90 (NF97)	
Material	Active Layer: Polyamide Support Layer/Paper: Polysulphone/Polyester					
MWCO	$\geq 200 \text{ Da}$		$\geq 200 \text{ Da}$		$\leq 200 \text{ Da}$	
Operating conditions	5 – 50 °C   15 – 42 (max. 55) bar   pH 3 – 10					
IEP	pH 4.3 <sup>a)</sup>		pH 4.12 – 4.42 <sup>b)</sup>		pH 4.1 <sup>c)</sup>	
Nominal retention	NaCl	76 % <sup>d)</sup>	NaCl	72 % <sup>d)</sup>	NaCl	$\geq 90 \%$
	MgSO <sub>4</sub>	$\geq 98 \%$	MgSO <sub>4</sub>	$\geq 98 \%$	MgSO <sub>4</sub>	$\geq 97 \%$
Pure water permeability	10 <sup>d)</sup>		9 – 18 <sup>d)</sup>		1 – 6 <sup>d)</sup>	
[kg m <sup>-2</sup> h <sup>-1</sup> bar <sup>-1</sup> ]	8.3 ± 0.2*		18.7 ± 0.8*		4.4 ± 0.5*	
[L m <sup>-2</sup> h <sup>-1</sup> bar <sup>-1</sup> ]*						

MWCO – molecular weight cut-off, IEP – isoelectric point

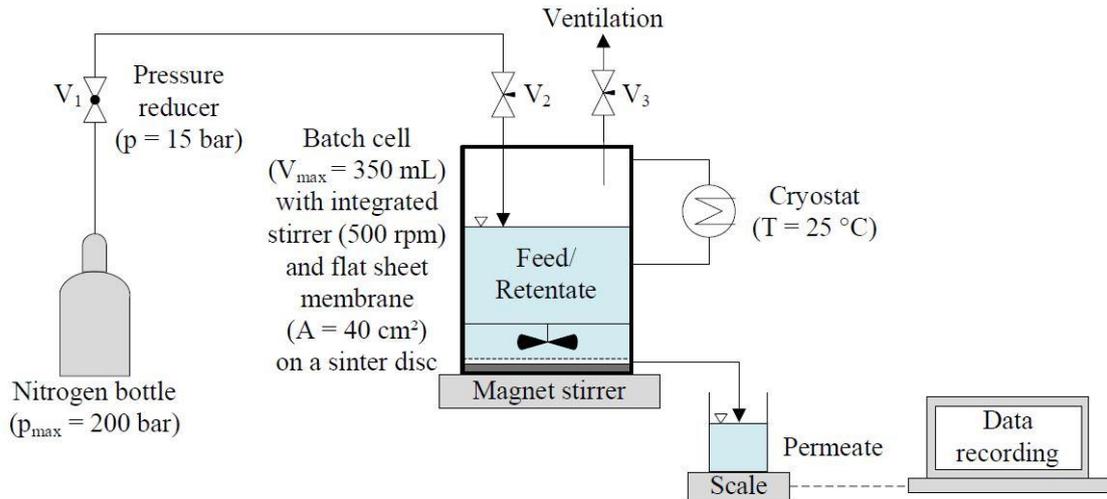
\*Measured with deionized water (15 bar, 25 °C, 500 rpm), calculated after Eq. 3

<sup>a)</sup>Nilsson et al. (2008), <sup>b)</sup>Oatley et al. (2012), <sup>c)</sup>Malmali et al. (2014), <sup>d)</sup>Restolho et al. (2009)

As can be seen in Table 1, the polymeric membranes are distinguished by their MWCO and therefore by their permeability and nominal retention towards mono- and divalent ions. Furthermore, the membranes have a positive, negative, or neutral zeta potential in dependence of pH, which can affect the retention mechanisms due to charge interactions.

### *pH-dependent nanofiltration experiments*

The membrane screening was conducted in dead-end set-up (see Figure 4) with a constant filtration pressure of 15 bar and constant temperature of 25 °C. The utilized thin-film composite flat-sheet membranes had an active surface area of 40 cm<sup>2</sup> and were pretreated for 45 min in Ultrasil<sup>®</sup>. All experiments were performed in double determination.



**Figure 4** Schematic presentation of the dead-end set-up.

Filtered permeate was let out pressureless and was weighted on a precision balance (Kern & Sohn GmbH, readout: 0.01 g). Similar to the feed, the composition of the permeate and retentate was analyzed by ICP-MS. The separation efficiency during filtration was evaluated by the retention, which was calculated according to Eq. 1 (see ‘mathematical equations’).

First, the pH-dependent single element retention of Ge, Mo, or Re was investigated with a recovery of 85.7 % (see Eq. 2). After a membrane preselection, the pH-dependent separation performance of the combined elements was examined, while testing different recoveries (25, 50, and 87.5 %). The aim of the investigations was to identify the optimal process conditions and a suitable membrane, which separates the combined elements from each other with a high selectivity and high permeability (see Eq. 3).

#### Mathematical equations

$$\text{Retention}[\%] = \left( 1 - \frac{c_{i,P}}{c_{i,R}} \right) \cdot 100 \% \quad (1)$$

$$\text{Recovery} [\%] = \frac{V_{P,t=\text{end}}}{V_{F,t=0}} \cdot 100 \% \quad (2)$$

$$\text{Permeability} [\text{L m}^{-2} \text{h}^{-1} \text{bar}^{-1}] = \frac{V_P}{A \cdot t \cdot p} \quad (3)$$

A – Membrane surface [m<sup>2</sup>]

c<sub>i</sub> – Concentration of element i [mg L<sup>-1</sup>]

V – Volume [L]

p – Pressure [bar]

t – time [h]

F – Feed

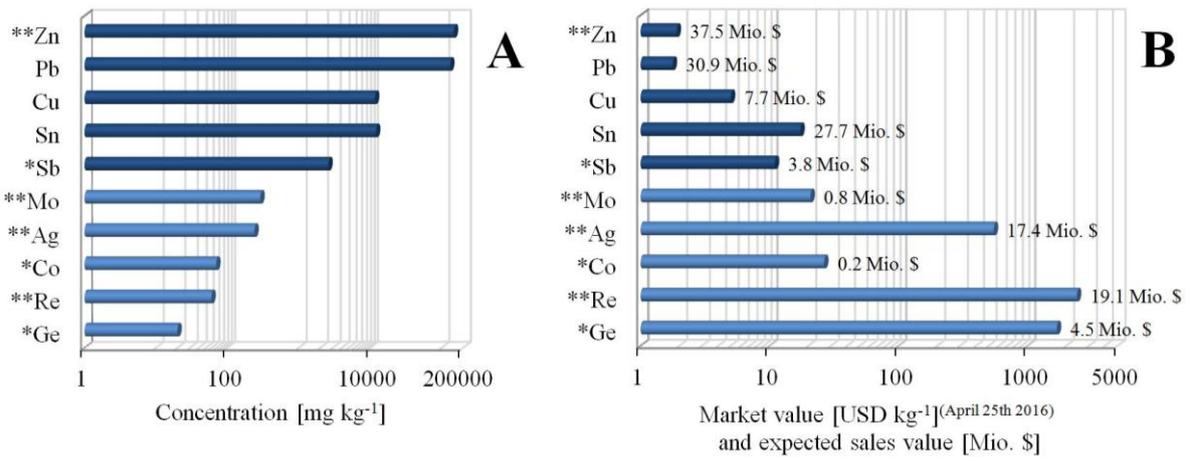
P – Permeate

R – Retentate

## Results and discussion

### The chemical composition of Theisenschlamm

The sampled Theisenschlamm was analyzed by EDXRF (Zn, Pb, Cu, Sn, Sb, Mo) and ICP-MS (Ag, Co, Re, Ge) to determine the chemical composition. Figure 5A shows the mean concentration values of selected elements. The current market value of these elements is illustrated in Figure 5B. Furthermore, the expected sales value was estimated.

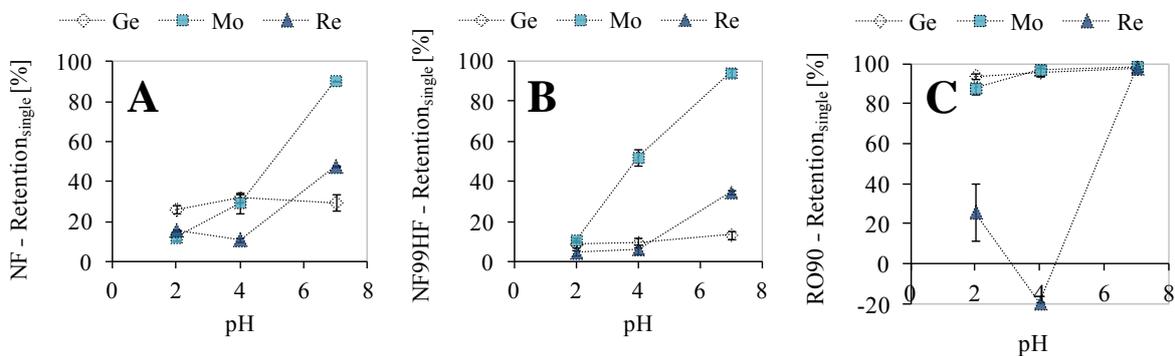


**Figure 5** (A) The chemical composition of Theisenschlamm (B) Current market value and expected sales value (assumed density 0.6 kg m<sup>-3</sup>); \*critical, \*\*candidate critical raw material (European Commission 2014).

Zinc and lead are the major components of Theisenschlamm (see Figure 5A). The market value of both elements is currently below 2 USD kg<sup>-1</sup>. However, the expected sales value exceeds 68 Mio. \$. As shown in Figure 2, zinc can be mobilized by bioleaching but it can be assumed that lead mainly remains as precipitate (PbSO<sub>4</sub>) as the leachate concentration is below 3 mg L<sup>-1</sup> (Klink et al. 2016). The solid concentration of the trace elements Mo, Ag, Co, Re, and Ge varies between 20 – 290 mg L<sup>-1</sup>. Silver is promising a high profit but similar to lead it seems to precipitate because the leachate concentration is little (1.4 µg L<sup>-1</sup>) (Klink et al. 2016). Therefore, the nanofiltration cannot be used as element-specific procedure to separate Ag. Rhenium and germanium are present in low concentration in the Theisenschlamm matrix but an extraction and separation seems worthwhile due to the high market value. The recovery of both elements shall be increased by mineral-specific bioleaching. On this assumption, nanofiltration experiments with 1 mg L<sup>-1</sup> Ge and 1 mg L<sup>-1</sup> Re were conducted. Furthermore, the pH-dependent separation performance of molybdenum (0.5 mg L<sup>-1</sup>) was investigated. Currently, only the separation performance of the anion-forming species is examined. Further investigations are aimed to extend the synthetic feed solution by the addition of other elements (e.g. Zn, Cu, Co).

*pH-dependent nanofiltration experiments*

The pH-dependent retention of the single elements Ge, Mo, and Re is illustrated in Figure 6A–C for the three tested polymeric membranes. Respective literature data is missing at the moment and the conducted research should clarify the influence of pH, MWCO, ionic species, and zeta-potential on the separation performance.



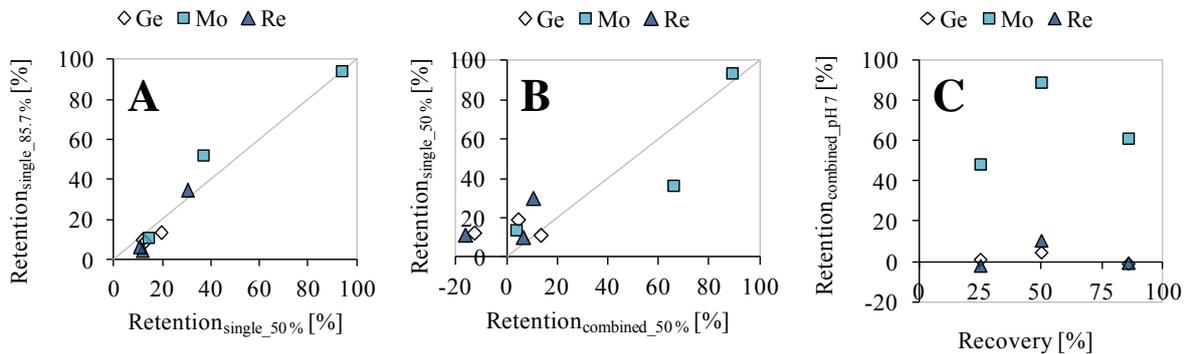
**Figure 6** The pH-dependent retention of the single element Mo (0.5 mg L<sup>-1</sup>), Ge (1 mg L<sup>-1</sup>), or Re (1 mg L<sup>-1</sup>) using the membrane (A) NF (B) NF99HF (C) RO90 (15 bar, 25 °C, 85.7 % recovery).

As shown in Figure 6A–C, the separation performance is obviously affected by the pH and the MWCO. The membrane RO90 (see Figure 6C) has the smallest MWCO and therefore, the highest Ge and Mo retention (>88 %). Germanium is present as Ge(OH)<sub>4</sub><sup>0</sup> in the investigated pH range (Pokrovski

and Schott 1998; Virolainen et al. 2013). For this reason, charge interactions can be excluded and convective transport mechanisms dominate here. The same applies for molybdenum at pH 2 because  $H_2MoO_4^0$  is present in the aqueous solution. With increasing pH, the ionic species is transforming into  $MoO_4^{2-}$  (Ozeki et al. 1988) and charge interactions become relevant as can be observed in Figure 6A and B. The molybdenum retention is significantly increasing (pH 7 >90 %) caused by repulsion between negatively charged membrane surface and the dominating  $MoO_4^{2-}$  anion above the isoelectric point. Different molybdenum retentions at pH 4 are attributable to the varying location of the IEP (see Table 1) and the more or less pronounced retention of the present ionic species.

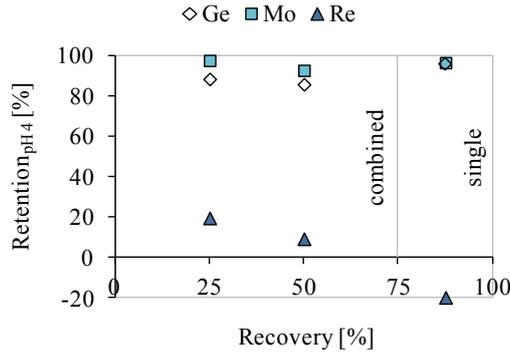
Rhenium is present as  $ReO_4^-$  in the investigated pH range (Magee and Blutstein 1985; Srivastava et al. 2015) and therefore charge interactions are more pronounced. Similar to Mo, the Re retention is enhanced at pH 7 due to repulsion, which can be seen in Figure 6A–C. Conspicuous is the low rhenium retention of the RO90 at pH 2 and 4 (see Figure 6C). Although this membrane has the smallest MWCO and Ge as well as Mo is rejected, Re can permeate nearly unimpeded. The IEP at pH 4.1 enables a convective transport without charge interferences and therefore, the Re retention is even lower than for the NF and NF99HF. At pH 2, an attraction of  $ReO_4^-$  towards the positively charged RO90 membrane surface seems more likely for the low Re retention.

According to the manufacturer’s information, the MWCO of the membranes NF and NF99HF should be similar but the experimental results conclude that the NF must have a smaller cut-off due to the fact that the retentions are increased compared to the NF99HF. However, derived from Figure 6B, it can be assumed that the selectivity of the NF99HF is even enhanced for the combined elements and a separation at pH 7 seems feasible. Before testing the separation performance of the combined elements for NF99HF (see Figure 7B), the single element retention was evaluated with a recovery of 50 % (see Figure 7A) because a lower recovery might improve the performance efficiency.



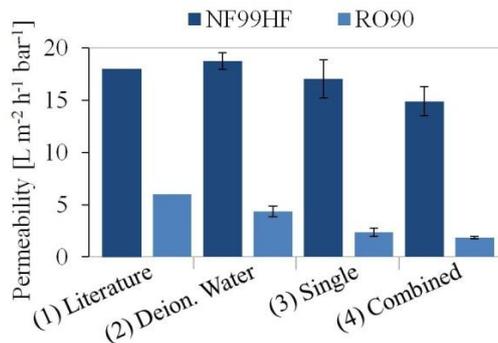
**Figure 7** (A) Retention of the single elements – varying recoveries (B) Single and combined element retentions – 50 % recovery (C) Retention of the combined elements at pH 7 – varying recoveries (NF99HF, 15 bar, 25 °C).

As can be seen in Figure 7A, the retention of the single elements is nearly unaffected by varying the recovery. However, if the elements got combined, the retentions are changing (see Figure 7B) caused by the Donnan equilibrium. The charged membrane strives towards electroneutrality and in case  $MoO_4^{2-}$  is rejected at pH 7, more  $ReO_4^-$  can permeate because the equilibrium needs to be established. Due to this fact, the recovery has a significant influence on the combination experiments as a concentration of the bulk solution forces the gradient of the chemical potential (Mulder 1996). This becomes clearly evident in Figure 7C. Neither a recovery of 25 or 85.7 % shows a satisfying separation selectivity. Using a recovery of 50 % enables a separation of Mo from the three-component solution. A separation of rhenium would be more desirable because the estimated sales value exceeds 19 Mio. \$. This seems feasible with the RO90 at pH 4 and can be seen in Figure 8.



**Figure 8** Retention of the single and combined elements testing different recoveries for the RO90 at pH 4 (15 bar, 25 °C).

Figure 8 shows that Re can be separated from Ge and Mo at pH 4 with the best efficiency using a recovery of 50 %. Combination experiments with a recovery of 85.7 % were not performed because the permeability was very low (see Figure 9). It can be assumed that the addition of divalent cations (e.g.  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Zn}^{2+}$ ) should not be detrimental for the rhenium separation because in general they have a high retention (Mulder 1996). For example, the manufacturer indicates that the  $\text{MgSO}_4$ -retention is above 97 % for the RO90. However, the presence of other monovalent metal anions (e.g.  $\text{Sb}(\text{OH})_6^-$ ) might be disturbing for the selective separation of Re but further combination experiments have to examine these hypothesis.



**Figure 9** Permeability of NF99HF and RO90 in comparison (1) Literature data from Table 1 (2) Deionized water (3) Single element feed solution (4) Combined element feed solution (15 bar, 25 °C).

The permeability of NF99HF and RO90, which was measured with deionized water, is similar to the literature data (see Figure 9). It was observed that the permeability is decreasing in case Ge, Mo, or Re was added to the feed solution. If the elements got combined, the decrease is even higher. The permeability of the NF99HF achieves higher values compared to the RO90 due to the enlarged MWCO. In the planned cross-flow set-up, the transmembrane pressure shall be increased and as consequence, the permeability should be enhanced especially for the RO90. The utilized dead-end set-up is restricted to 20 bar.

### Conclusion

The influence of pH (2, 4, 7) on the retention of the single and combined strategic elements Ge, Mo, and Re by nanofiltration using three different polymeric membranes (Alfa Laval: NF, NF99HF, RO90) was studied. The NF ( $\geq 200$  Da) and NF99HF ( $\geq 200$  Da) show a similar separation performance but the selectivity of the NF99HF is increased. Currently, Mo can be separated from Re and Ge at pH 7 using the NF99HF. The highest Ge and Mo retention ( $>88\%$ ) was measured for the RO90 due to the smallest MWCO ( $\leq 200$  Da). Nevertheless, this membrane shows a high selectivity towards rhenium, which can be separated from the synthetic multicomponent solution at pH 4. However, the permeability of the RO90 was below  $2 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$  in the combination experiments but it can be assumed that a higher filtration pressure will lead to an increased permeability. This will be verified in further cross-flow experiments.

The following dead-end investigations are aimed to examine the retention mechanisms of Co, Cu, and Zn in single element experiments and in combination with Ge, Mo, and Re using the NF99HF. Moreover, other membrane materials like polyethersulfone shall be screened. Furthermore, cross-flow experiments shall be conducted to verify the dead-end results and to receive reliable data for a scale-up. The ascertained data shall be processed in a mathematical model to predict retention mechanisms, even for similar separation problems. Multicomponent solutions could be treated by a nanofiltration membrane, which was intended as suitable in advance.

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