

**Selective Separation of the Strategic Elements
Germanium and Rhenium from
Multicomponent Leaching Solutions
by Nanofiltration**

vorgelegt von
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*“We think of our land and water and human resources
not as static and sterile possessions but as life giving
assets to be directed by wise provisions for future days.”*

Franklin D. Roosevelt

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Katja Meschke

Abstract

For decades, membranes have been utilized for aqueous solution treatment and hence, they seem suitable for the separation of strategic elements from complex leaching solutions. This work focuses on germanium and rhenium, which are required for high-tech products. Therefore, the demand is steadily increasing on a global scale. Considerable amounts of both elements are present in Theisen sludge, a waste by-product from German copper ore smelting. Via biohydrometallurgical leaching, the valuable elements can be mobilized from the solid phase. Afterwards, the complex solution required processing by nanofiltration. Therefore, the separation mechanisms of strategic elements and the effect of pH, membrane characteristics, and process parameters are investigated in this work. By adjusting pH and other process parameters, the separation of germanium and rhenium from the multicomponent leaching solution is influenced and achieved. In conclusion, a potential process chain for a scale-up to separate the investigated strategic elements is presented.

Kurzfassung

Membranen werden seit Jahrzehnten zur Aufbereitung wässriger Stoffsysteme eingesetzt, weshalb sich diese zur Abtrennung strategischer Elemente aus komplexen Laugungslösungen eignen können. Im Fokus dieser Arbeit stehen Germanium und Rhenium, die zur Fertigung von High-Tech Produkten benötigt werden und deren Nachfrage weltweit stetig steigt. Beträchtliche Mengen der beiden Elemente befinden sich im Theisenschlamm, einem Abfallprodukt der deutschen Kupferschieferverschüttung. Durch biohydrometallurgisches Laugen können die Wertelemente in die wässrige Phase überführt werden. Im Anschluss daran soll die komplexe Lösung mittels Nanofiltration aufbereitet werden. Aus diesem Grund werden die Trennmechanismen der strategischen Elemente, sowie der Einfluss des pH-Wertes, der Membraneigenschaften und Prozessparameter auf das Trennverhalten, im Rahmen dieser Arbeit untersucht. Durch die Variation von pH sowie der Prozessparameter, kann die Trennung von Germanium und Rhenium aus der Multikomponenten-Laugungslösung beeinflusst und realisiert werden. Darüber hinaus wird eine mögliche Prozesskette für ein Scale-up, zur Separation der untersuchten strategischen Elemente vorgestellt.

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List of Publications

This cumulative dissertation is based on four peer-reviewed publications:

Chapter 3

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Chapter 4

K. Meschke, N. Hansen, R. Haseneder, J.-U. Repke. Characterization and performance evaluation of polymeric nanofiltration membranes for the separation of strategic elements from aqueous solutions. *J. Membr. Sci.* 546 (2018) 246–257.

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Chapter 5

K. Meschke, N. Hansen, R. Hofmann, R. Haseneder, J.-U. Repke. Influence of process parameters on separation performance of strategic elements by polymeric nanofiltration membranes. *Sep. Purif. Technol.* 235 (2020) 116186.

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Chapter 6

K. Meschke, R. Hofmann, R. Haseneder, J.-U. Repke. Membrane treatment of leached mining waste—a potential process chain for the separation of the strategic elements germanium and rhenium. *Chem. Eng. J.* 380 (2020) 122476.

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Abbreviations and Symbols

Abbreviations

Abbreviation	Description
AFM	Atomic force microscopy
ATR-FTIR	Attenuated total reflection - Fourier Transform Infrared Spectroscopy
approx.	Approximate
aq.	Aqueous
BMBF	Bundesministerium für Bildung und Forschung
CRD	Compact rotating disc
CRM	Critical raw material
DSPM-DE	Donnan steric pore model (and) dielectric exclusion (model)
EU	European Union
HIF	Helmholtz-Institut Freiberg für Ressourcentechnologie
HZDR	Helmholtz-Zentrum Dresden-Rossendorf
e.g.	Exempli gratia
ICP-AES	Inductively Coupled Plasma - Atomic Emission Spectrometry
ICP-MS	Inductively Coupled Plasma - Mass Spectrometry
IEP	Isoelectric point
MF	Microfiltration
MW	Molecular weight
MWCO	Molecular weight cut-off
n. a.	Not available
NF	Nanofiltration
PA	Polyamide
PES	Polyethersulfone
PLS	Pregnant leaching solution
PPA	Poly(piperazine)amide
RO	Reverse osmosis
SEM	Scanning electron microscopy
SHM	Schwertmannite
SHP	Steric hindrance pore (model)
tetr.	Tetrahedral
TM	Transport model
TMP	Transmembrane pressure
TOC	Total organic carbon
TU	Technische Universität
UF	Ultrafiltration
UFZ	Umweltforschungszentrum
WP	Work package

Symbols – Latin Letters

Letter	Description	Unit
a	Activity coefficient	–
A	Membrane surface area	m^2
A_k	Porosity of the membrane active layer	–
c	Concentration	$\text{mol m}^{-3}/\text{mg L}^{-1}$
d	Diameter	m
D	Diffusion coefficient	–
E	Electrochemical potential	J mol^{-1}
E_h	Redox potential	V
F	Faraday constant	C mol^{-1}
J	Permeate flux	$\text{mol m}^{-3} \text{s}^{-1}/\text{kg m}^{-2} \text{h}^{-1}$
K	Hindrance factor for convection	–
k_s	Specific conductivity of the solution	S m^{-1}
L	Permeability	$\text{kg m}^{-2} \text{h}^{-1} \text{bar}^{-1}$
L	Proportional coefficient	–
m	Mass	kg
$\dot{m}$	Mass flow	kg h^{-1}
MW	Molecular weight	g mol^{-1}
$MWCO$	Molecular weight cut-off	Da
N	Rotational speed	min^{-1} or rpm
p	Pressure	bar
R	Ideal gas constant	$\text{J mol}^{-1} \text{K}^{-1}$
R	Resistance	Ωcm^{-2}
R	Retention	%
R	Roughness	nm
r	Radius	nm
s	Thickness	m
S	Mean plane of the surface	nm
T	Temperature	K
T	Time	h
TMP	Transmembrane pressure	bar
V	Volume	L
$\dot{V}$	Volume flow	L h^{-1}
w/w	Weight percent	%
x	Horizontal dimension	nm
z	Vertical dimension	nm
z	Charge number/valence	–
ΔE	Streaming potential	V
ΔP	Transmembrane pressure	bar
Δx	Effective thickness of the active layer	nm

Symbols – Greek letters

Letter	Description	Unit
δ	Thickness	nm
ε	Dielectric permittivity	A s V ⁻¹ m ⁻¹
η	Dynamic viscosity of the solution	Pa s
λ	Ratio between r_s and r_p	–
μ	Chemical potential	kJ mol ⁻¹
v	Solute velocity	m s ⁻¹
$\tilde{v}$	Molar volume	m ³ kmol ⁻¹
ζ	Zeta potential	V
σ	Reflection coefficient	–
φ	Local electrical potential inside pore	V
Φ	Steric partitioning coefficient	–
ψ	Electric potential	V

Symbols – Indices

Indices	Description
<i>a</i>	Average
<i>B</i>	Bulk
<i>c</i>	Cake
<i>c</i>	Convective
<i>d</i>	Diffusive
<i>e</i>	Electromigrative
<i>F</i>	Feed
<i>h</i>	Hydrated
<i>i</i>	Component/ion
<i>i</i>	Inner
<i>lim</i>	Limiting
<i>m</i>	Membrane
<i>max</i>	Maximum
<i>o</i>	Outer
<i>p</i>	Pore
<i>p</i>	Peripheral
<i>P</i>	Permeate
<i>R</i>	Retentate
<i>s</i>	Solute
<i>t</i>	Time
<i>w</i>	Water
0	Reference state
50	Distribution at 50%

Chemical formula

Formula	Description
<i>Ag</i>	Silver
<i>Ag₈GeS₆</i>	Argyrodite
<i>Al</i>	Aluminum
<i>α-Al₂O₃</i>	Aluminum oxide
<i>As</i>	Arsenic
<i>Au</i>	Gold
<i>Cd</i>	Cadmium
<i>Cl⁻</i>	Chloride ion
<i>Co</i>	Cobalt
<i>Co²⁺</i>	Divalent cobalt cation
<i>-COO⁻</i>	Carboxylate anion group
<i>-COOH</i>	Carboxyl group
<i>Co(OH)⁺</i>	Hydroxo cobalt ion
<i>Co(OH)₂</i>	Cobalt hydroxide
<i>CoSO₄ · 7H₂O</i>	Cobalt(II) sulfate heptahydrate
<i>Cr</i>	Chromium
<i>Cu</i>	Copper
<i>Cu²⁺</i>	Divalent copper cation
<i>Cu(OH)₂</i>	Copper hydroxide
<i>CuFeS₂</i>	Chalcopyrite
<i>Cu₁₃Fe₂Ge₂S₁₆</i>	Germanite
<i>CuSO₄</i>	Copper(II) sulfate
<i>Fe</i>	Iron
<i>Fe²⁺</i>	Ferrous iron
<i>Fe³⁺</i>	Ferric iron
<i>FeAsS</i>	Arsenopyrite
<i>FeS₂</i>	Pyrite
<i>FeSO₄</i>	Iron sulfate
<i>Fe₂(SO₄)₃</i>	Iron(III) sulfate
<i>Ga</i>	Gallium
<i>Ge</i>	Germanium
<i>GeO</i>	Germanium oxide
<i>GeO₂</i>	Germanium(IV) dioxide
<i>Ge(OH)₄⁰</i>	Germanic acid
<i>GeO(OH)₃⁻</i>	Germanium oxoanion
<i>GeS</i>	Germanium sulfide
<i>H⁺</i>	Hydrogen ion
<i>HMoO₄⁻</i>	Hydrogen molybdate
<i>H₂MoO₄⁰</i>	Molybdic acid
<i>HNO₃</i>	Nitric acid
<i>H₂O</i>	Water

Formula	Description
$HReO_4$	Perrhenic acid
HSO_4^-	Hydrogen sulfate
H_2SO_4	Sulfuric acid
In	Indium
$Me(OH)^+$	Hydroxo metal ion
MeS	Metal sulfide
$MeSO_4$	Metal sulfate
Mg	Magnesium
Mg^{2+}	Divalent magnesium cation
$MgSO_4$	Magnesium sulfate
Mn	Manganese
Mo	Molybdenum
MoO_4^{2-}	Molybdate
Na^+	Sodium ion
$NaCl$	Sodium chloride
$NaHCO_3$	Sodium bicarbonate
$Na_2MoO_4 \cdot 2H_2O$	Sodium molybdate(VI) dihydrate
$NaOH$	Sodium hydroxide
$NaReO_4$	Sodium perrhenate(VII)
Na_2SO_4	Sodium Sulfate
$-NH_3$	Amino group
Ni	Nickel
O_2	Oxygen
$-OH$	Hydroxyl group
Pb	Lead
PbS	Galena (lead sulfide)
PO_4^{3-}	Phosphate ion
Re	Rhenium
ReO_4^-	Perrhenate
S	Sulfur
Sb	Antimony
Si	Silicon
Sn	Tin
$-SO_2$	Sulfonyl group
$-SO_3^-$	Sulfonate group
SO_4^{2-}	Sulfate ion
Ti	Titan
Tl	Tellurium
U	Uranium
V	Vanadium
W	Tungsten
Zn	Zinc
Zn^{2+}	Divalent zinc cation

Formula	Description
ZnS	Sphalerite (zinc sulfide)
$\beta\text{-}ZnS$	Wurtzite
$Zn(OH)^+$	Hydroxo zinc ion
$Zn(OH)_2$	Zinc hydroxide
$ZnSO_4 \cdot H_2O$	Zinc(II) sulfate monohydrate
Zr	Zirconium

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1. Introduction and Motivation

For all industrial nations, access and supply of raw materials to manufacture existing and develop emerging technologies is of prime importance. The European Union (EU) has merely a limited supply of primary resources due to geological conditions and thus, the recovery of secondary resources becomes more acute for a safe supply. An old mining residue, the so-called Theisen sludge – a scrubbed flue dust from copper ore smelting, represents a potential feedstock for secondary metal processing and refining. This material is accessed by a proposed hybrid process (see Figure 1.1), combining the hydrometallurgical technique of bioleaching with separation and concentration methods such as solvent extraction, adsorption, and membrane treatment, leading to metal recovery and separation.

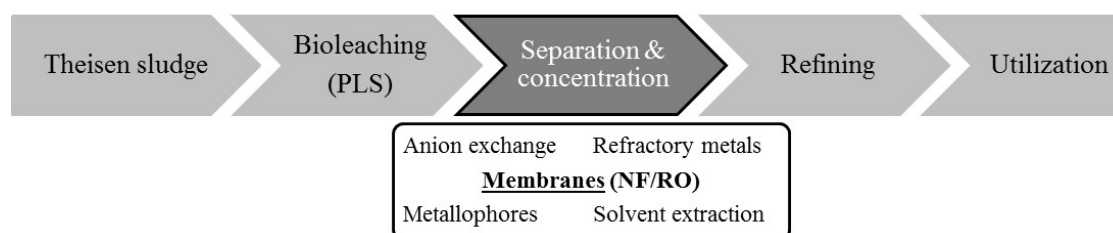


Figure 1.1. Proposed processing of Theisen sludge to mobilize, separate, and concentrate strategic elements (PLS – pregnant leaching solution, NF – nanofiltration, RO – reverse osmosis) [1].

Via bioleaching, the bonded metals are mobilized but the resulting pregnant leaching solution (PLS) is highly complex due to the acidic multicomponent character on a wide range of concentrations and thus, downstream processing is hampered. The present work explores the potential of membranes, in particular the separation of the strategic elements germanium (*Ge*) and rhenium (*Re*) from the bioleachate by nanofiltration (NF). Moreover, reverse osmosis (RO) is investigated for element concentration (see Figure 1.1). The theoretical background considered in this work is detailed in chapter 2.

This cumulative thesis is based on four accepted peer-reviewed publications (see chapter ‘List of Publications’), including the following subjects:

In chapter 3, the feedstock Theisen sludge and the performed bioleaching is described. Furthermore, nanofiltration is focused and thus, the fundamental pH-dependent separation performance of the elements *Ge* and *Re*, which is determined for three different commercial NF membranes (NF99HF, UTC-60, NP010) in dead-end set-up. Next, the recovery of *Mo* and the cationic transition metals *Co*, *Cu*, and *Zn* is investigated and their influence on the separation selectivity. For all investigations, model solutions were

utilized. Thereby, the element concentrations and pH are based on the real bioleaching solution.

Following, membrane characteristics such as roughness, hydrophilicity, and zeta potential are determined and their influence on the separation performance investigated (see chapter 4). Therefore, two of the original three nanofiltration membranes (NF99HF, UTC-60) are utilized and the separation behavior screened with deionized water, *NaCl*, *MgSO₄*, and a model leaching solution containing *Ge*, *Mo*, *Re*, *Co*, *Cu*, and *Zn* in cross-flow set-up.

The process parameters (transmembrane pressure, flow velocity, flow regime, recovery, ionic strength) and their influence on the separation performance are investigated in chapter 5 in a cross-flow setup. On the basis of preceding experiments, eight promising commercial polymeric nanofiltration membranes are utilized to investigate the influence of transmembrane pressure using a model bioleaching solution. In the subsequent experiments, NF99HF is utilized due to high selectivity regarding *Ge* and *Re* and high permeability.

In chapter 6, the envisioned membrane downstream processing by membranes is presented, which was developed in consideration of the results obtained in chapter 3–5. Thereby, microfiltration is combined with nanofiltration and reverse osmosis. Microfiltration is investigated for Theisen sludge particle removal and getting a sterile solution. The conducted nanofiltration and reverse osmosis should ensure the separation of target element *Ge* and *Re* from the multicomponent leaching solution.

In the final discussion (see chapter 7), the results of this cumulative thesis (chapter 3–6) are summarized and discussed. The findings of this thesis and further research objectives are presented in ‘Conclusion and Outlook’ (see chapter 8) and indicate that a separation of *Ge* and *Re* is feasible and the utilized membranes are suitable for an acidic solution treatment and thus, the objective of this thesis was met. The results obtained close a former research gap and represent the starting point for technical up-scaling.

2. Theoretical Background

2.1 Mineral Raw Materials

Mineral-derived elements are important for current and emerging technologies [2] and thus, demand and prices are increasing globally [2,3]. As a consequence, fear of scarcity and supply bottlenecks are enhanced. Therefore, some raw materials were indicated as critical [3] but the criticality varies depending on industry, nation, and over time [2]. In 2017, the European Commission identified 27 critical raw materials (CRM), which have a high economic importance and high supply risk for the EU [4]. Figure 2.1 shows a part of these CRMs as well as potential CRMs, which are included in an old German mining residue (Theisen sludge, see section 2.3), the feedstock in this work.

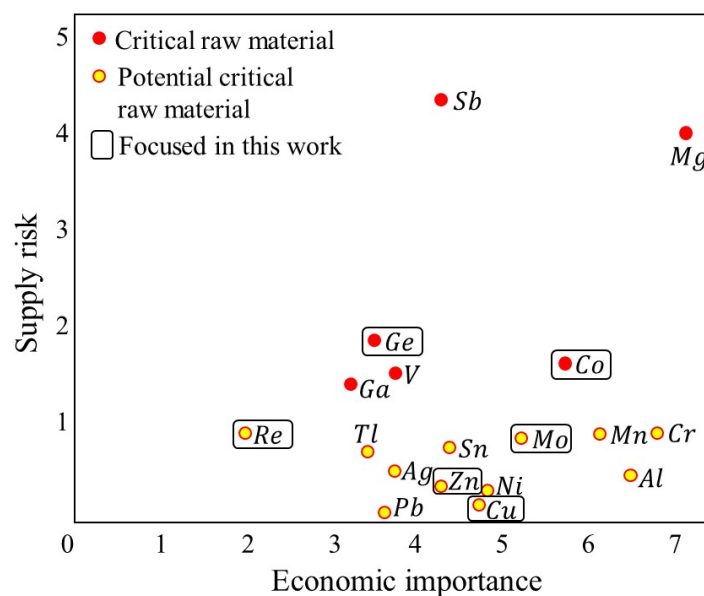


Figure 2.1. Critical and potential critical raw materials identified for the European Union in 2017, which are included in Theisen sludge [4,5].

To ensure a secure supply, natural resources must be exploited and valuable anthropogenic waste has to be reclaimed. At the latter, secondary resources such as landfills and mining residues are moved into focus and thus, mineral raw materials can be provided sustainably. Nevertheless, landfill and secondary mining is often associated with a great effort during downstream processing because the valuables are usually present at low concentrations and heterogeneously distributed within a complex matrix. Therefore, further processing often becomes uneconomic. The present work focuses on mining residues such as flue dust and slag, which are by-products from pyrometallurgical processes and usually enriched in metals. If the residuals have a fine-grained and sulfidic composition, biohydrometallurgical processes (see section 2.2) can be applied for metal

mobilization [6]. In this work, the separation of *Ge* and *Re* by membranes is focused (see section 2.4 and chapter 3–6). Both elements are present in a deposited flue dust (see section 2.3), rendering it a high economic value resource.

2.1.1 Germanium

C. Winkler discovered germanium (*Ge*) in 1886 in Freiberg, Saxony, Germany [7,8]. It has a greyish-white color and a metallic appearance. The physical properties of *Ge* are in a large number metallic. Regarding the electrical properties, it ranges between an isolator and a metal [8,9]. From a chemical point of view, *Ge* is very similar to *Si*. Therefore, it is often found in silicate minerals because *Si(IV)* can be substituted by *Ge(IV)* [9]. In nature, the only *Ge*-containing minerals in existence are argyrodite (Ag_8GeS_6 , 6–7% *Ge*) and germanite ($Cu_{13}Fe_2Ge_2S_{16}$, 8.7% *Ge*) [7]. Moreover, *Ge* is often associated in *Zn* ores and minerals and thus, widely dispersed in the earth crust with an average concentration of 1.5 ppm [10].

The technical application of crystalline *Ge* are found in infrared optics industry, where it is utilized for lenses and windows. Moreover, it is required for detectors (gamma radiation) and as substrate for opto-electronic devices due to high mechanical strength and crystallographic perfection. In these applications, *Ge* is processed in wafers and solar cells [7].

The required *Ge* is produced as by-product in hydrometallurgical or pyrometallurgical processes of *Zn*, *Cu*, and *Pb* ores and coals [7,11]. The *Ge* concentration in the exploited deposits can vary from hundredths to thousandths of a percent [11]. The volatilizing *Ge* (*GeO* or *GeS*) via pyrometallurgy leads to 1–6% in the produced concentrate [7]. If *Ge* is produced by hydrometallurgy, the *Ge* source (e.g. fly ash) has to include *GeO*₂, which is water soluble and can be extracted by leaching and concentrated by solvent extraction afterwards [10].

In 2016, the price of *GeO*₂ ranged between 690–720 US \$ kg⁻¹ [10]. Between 2018–2019, an average price of 735 US \$ kg⁻¹ [12,13] was listed on the stock exchange and thus, the prices were quite stable in the recent years. The main supplier of *Ge* is China by reason of geological conditions. The supply by other contributors, such as Canada estimates in sum only 25%. Nowadays, the recycling of products from the optical fiber industry becomes more relevant for *Ge* production [7]. An estimated 30% of the *Ge* used globally is derived from recycled material [7,10].

If *Ge* shall be extracted from a mining residue by leaching (see section 2.2), as investigated in this work, the speciation of the dissociation products within the aqueous solution is of high interest for the subsequent separation processes (e.g. nanofiltration, solvent extraction). Therefore, speciation and phase diagrams are required for interpretation to select the best fitting downstream process. The pH-dependent species distribution diagram of *Ge* is shown in Figure 2.2, which illustrates the fractions formed in water.

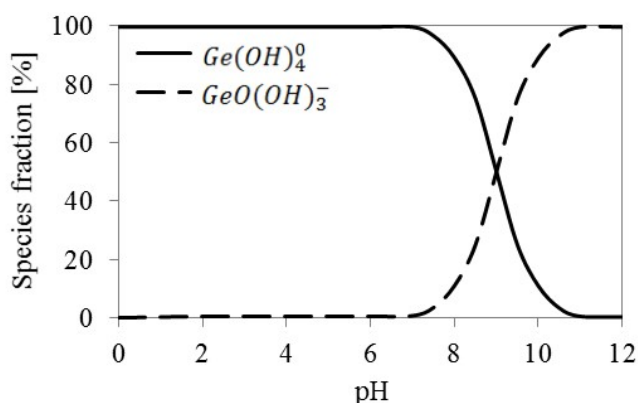


Figure 2.2. pH-dependent species distribution diagram for *Ge*(IV) (germanium-water at 25°C) [14].

In water GeO_2 (tetr) reacts to germanic acid $Ge(OH)_4^0$ (aq) under neutral and acidic conditions (see Figure 2.2). Thereby, the solubility is independent of pH (pH 1–8), oxygen fugacity, and ionic strength. Above pH 8, the neutral *Ge* species dissociates and the anion $GeO(OH)_3^-$ is formed, which is predominant under alkaline conditions [14]. However, the neutral species $Ge(OH)_4^0$ will be dominant in the acidic leaching solution. As the separation of *Ge* shall be realized by nanofiltration, the radius of $Ge(OH)_4^0$ is of high interest to interpret steric transport through the membrane. In the presence of $GeO(OH)_3^-$, charge interactions become relevant for separation performance. In chapter 3, the influence of pH is investigated and discussed.

2.1.2 Rhenium

The last natural element discovered was rhenium (*Re*) in 1925 in Germany by W. Noddack, I. Tacke, and O. Berg [15,16]. The concentration in the earth's crust typically ranges between 0.7–1 ppb [15]. Similar to *Ge*, no specific metallogical species can be found. Mostly, it is distributed in porphyry molybdenum-copper deposits and reaches concentrations of up to 0.2% [15,16].

Re is considered a refractory metal with unique properties including the second highest melting point (approx. 3200°C) and a high specific gravity [15]. Therefore, it is an essential part of the superalloy industry and utilized for specialist technologies such as aviation, aerospace, and catalyst industry [16,17]. More than 80% of the *Re* produced globally is required for industrial gas and superalloy turbines [18].

Re is a by-product of pyrometallurgical processes from *Cu*, *Pb*, and *U* extraction. The accruing top gas is purified and passed to sulfuric acid production. Afterwards, *Re* is concentrated up to 30% by solvent extraction [17]. Moreover, hydrometallurgical processes such as bioleaching, pressure oxidative leaching, and acidic-salt decomposition are applied for *Re* extraction [19]. An estimated 52.6 t of *Re* were produced in 2012, primarily in Chile (51%) due to large porphyry deposits [20]. Predictions expect a 7% grow of the global *Re* market between 2019–2022 [18]. In August 2008, the *Re* price reached a peak of 12000 US \$ kg⁻¹ due to enhanced demand for aerospace engineering. Afterwards, the price dropped to 4000 US \$ kg⁻¹ until 2012. Prior to peaking (1998–2000), the prices were relatively stable between 300–1500 US \$ kg⁻¹ [21]. This level is reached again and the prices fluctuate around 1000–1500 US \$ kg⁻¹ since 2017 [22].

Similar to *Ge*, the ionic species of *Re* in an aqueous solution (see Figure 2.3) must be known to choose an adequate separation and concentration process after hydrometallurgical leaching.

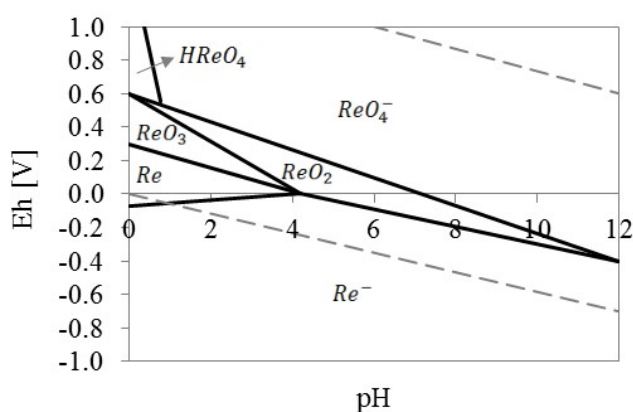


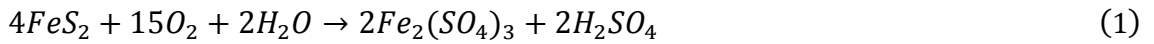
Figure 2.3. *Eh-pH-dependent diagram for Re(VII) (rhenium-water system at 25°C) [23].*

As shown in Figure 2.3, mainly in an oxidic environment (positive redox potential), the dominant species over the whole pH range is perrhenate (ReO_4^-), except at pH < 1 with perrhenic acid (HReO_4) as predominant species [23]. During bioleaching (see section 2.2), the redox potential is highly positive (approx. 400–700 mV [24,25]) to realize the biooxidation of metal sulfides [26]. Therefore, the mobilized *Re* will be present

as monovalent anion in the acidic bioleaching solution. As consequence, the separation by nanofiltration will mainly be affected by charge interactions. The pH-dependent separation performance of ReO_4^- is investigated and discussed in chapter 3.

2.2 Bioleaching (Biohydrometallurgy)

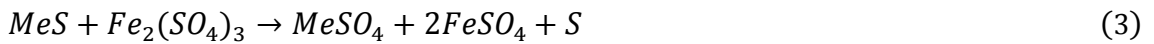
Biohydrometallurgical processes such as bioleaching present an alternative to pyrometallurgy. The leaching process involves the dissolution of sulfide minerals by oxidation via bacteria [25]. The most extensively utilized bacteria for commercial use are the genus *Acidithiobacillus* (*ferrooxidans* and *thiooxidans*) and *Leptospirillum* (*ferrooxidans*), which are chemolithoautotrophic and grow under mesophilic (25–35°C) and acidic (pH 1.5–3) conditions [24,27]. The metals can be dissolved from mineral concentrates or low-grade ores by direct and indirect leaching mechanisms. Moreover, leaching may be utilized for metal recovery from mining and industrial waste. Via direct contact leaching, the bacteria interact with the mineral surface (enzymatic attack) and oxidize the sulfide phase [25,27] as shown in Eq. 1 for pyrite (FeS_2) [27].



For non-ferrous metal sulfides (MeS) such as sphalerite (ZnS) and galena (PbS), the direct oxidation can be summarized according Eq. 2 [27].



In contrast, the bacteria generate a lixiviant in indirect bioleaching, which oxidizes the metal sulfides. Under acidic conditions, ferric iron (Fe^{3+}) is this lixiviant (see Eq. 3 and 4) and bacteria (*ferrooxidans*) can reoxidize the arising ferrous iron (Fe^{2+}) to ferric iron, needed for oxidation again [25,27].



The generated sulfur is oxidized by bacteria to sulfuric acid as shown in Eq. 5. and thus, acidic conditions are created for ideal bacteria grow [27].



Summing up, bioleaching is an interaction of chemical and biological oxidation and direct and indirect leaching mechanisms always occur in parallel [27]. Via low-cost processes such as in situ dump and heap leaching, the industrial extraction can be realized [25]. Furthermore, ex situ leaching in stirred tank reactors is feasible [26]. Globally, the

bacterially-assisted leaching is extensively applied, especially for copper (Cu) extraction from chalcopyrite ($CuFeS_2$) and gold (Au) from gold-bearing arsenopyrite ($FeAsS$) [25,26]. The present work focuses on the mobilization of the strategic elements Ge and Re from a mining residue (Theisen sludge).

2.3 Case Study Theisen Sludge

A German mining residual from copper ore smelting, the so-called Theisen sludge (German: Theisenschlamm) is the focus of the present work. The copper shale ore was mined and processed in Central Germany in a shaft furnace in the late 19th century. Next to polymetallic copper stone and slag, the ore smelting generated a flue dust, which was scrubbed from the furnace top gas. The flue dust was suspended in water, dewatered, and stored in basins for further treatment. After German reunification, in 1990, the copper ore mining was abandoned and approx. 220000–330000 t of Theisen sludge were deposited in about 2000 unsealed ponds and basins [28,29]. In the 90s, the sludge was disposed in a central mono-landfill (pond 10, see Figure 2.4) in Helbra, Saxony-Anhalt, Germany [29,30].

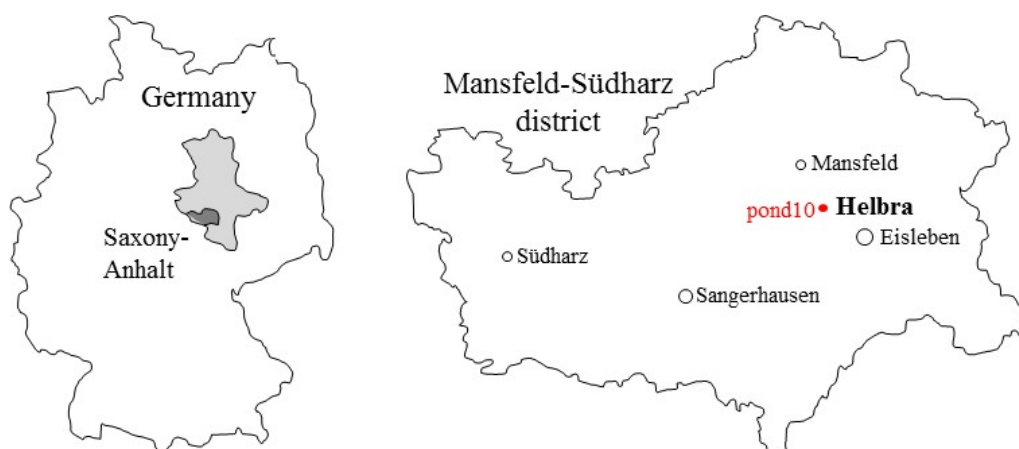


Figure 2.4. Location of the Theisen sludge mono-landfill pond 10 (Helbra, Saxony-Anhalt, Germany).

The Theisen sludge has a mineral sulfidic composition, is fine-grained (median diameter: 1.25 μm , mean diameter: 1.55 μm) and enriched with heavy metals (e.g. 18% Zn , 14% Pb) as well as organic pollutants [28,30]. Since 1978, various pyrometallurgical and hydrometallurgical processes have been developed to extract valuable elements from the sludge but none of them were economic [6,28].

The interdisciplinary r⁴-joint project (“Winning of economically strategic materials from fine-grained residues from copper smelting – Theisenschlamm”, Project number:

033R137, duration of project: 2/2015–1/2018) funded by Germany's Federal Ministry of Education and Research (BMBF) aimed at investigating to develop an environmentally friendly, energy-efficient, and profitable hybrid process for the recovery of elements with economic relevance included in the Theisen sludge [31,32]. An overview of the r^4 -project and participating partners is shown in Figure 2.5.

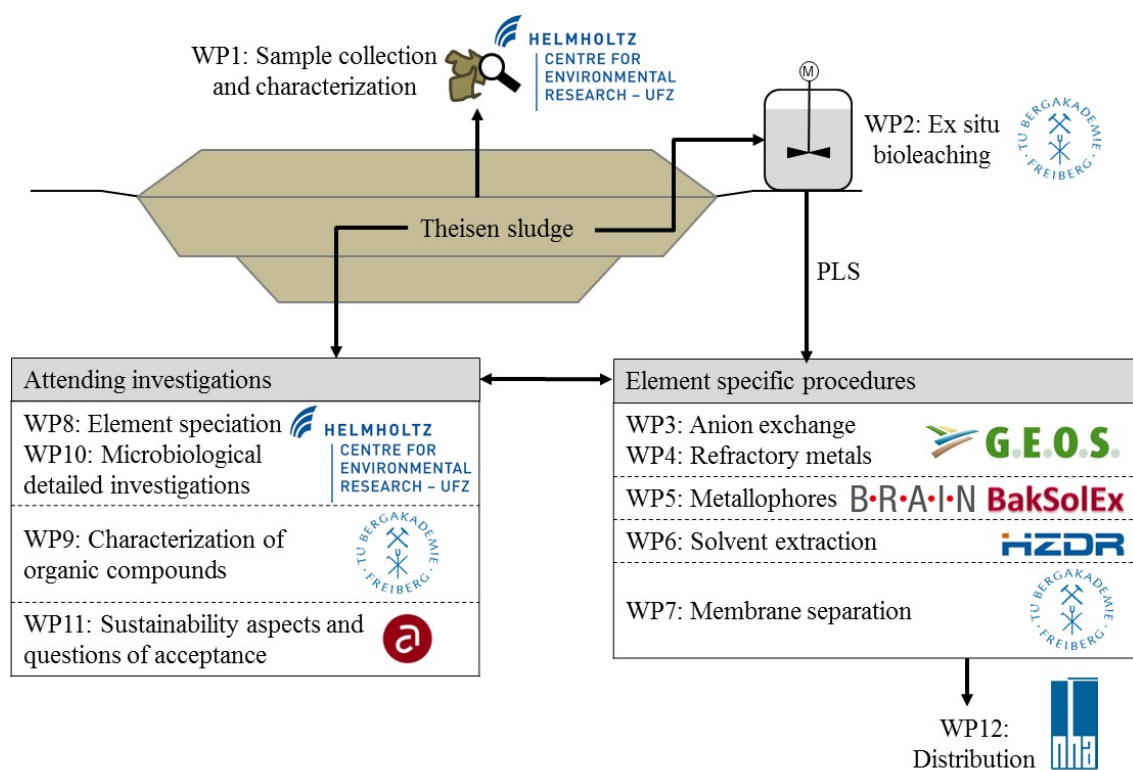


Figure 2.5. Overview of the r^4 -joint project "Theisenschlamm" (PLS – pregnant leaching solution, WP – work package).

At the beginning of the r^4 -project, Theisen sludge (see Figure 2.6) was sampled from the mono-landfill by the Department of Analytical Chemistry at the Helmholtz Center for Environmental Research (UFZ, WP1). Via X-ray fluorescence analysis, the chemical composition of the solid matter was established. Moreover, an aqua regia digestion with ICP-MS and ICP-AES analysis was conducted to detect trace elements in the complex sludge matrix [6,33]. The determined composition of Theisen sludge is shown in Figure 2.7.



Figure 2.6. Theisen sludge sample from the mono-landfill pond 10 (Helbra, Saxony-Anhalt, Germany, picture: Birgit Daus (UFZ)).

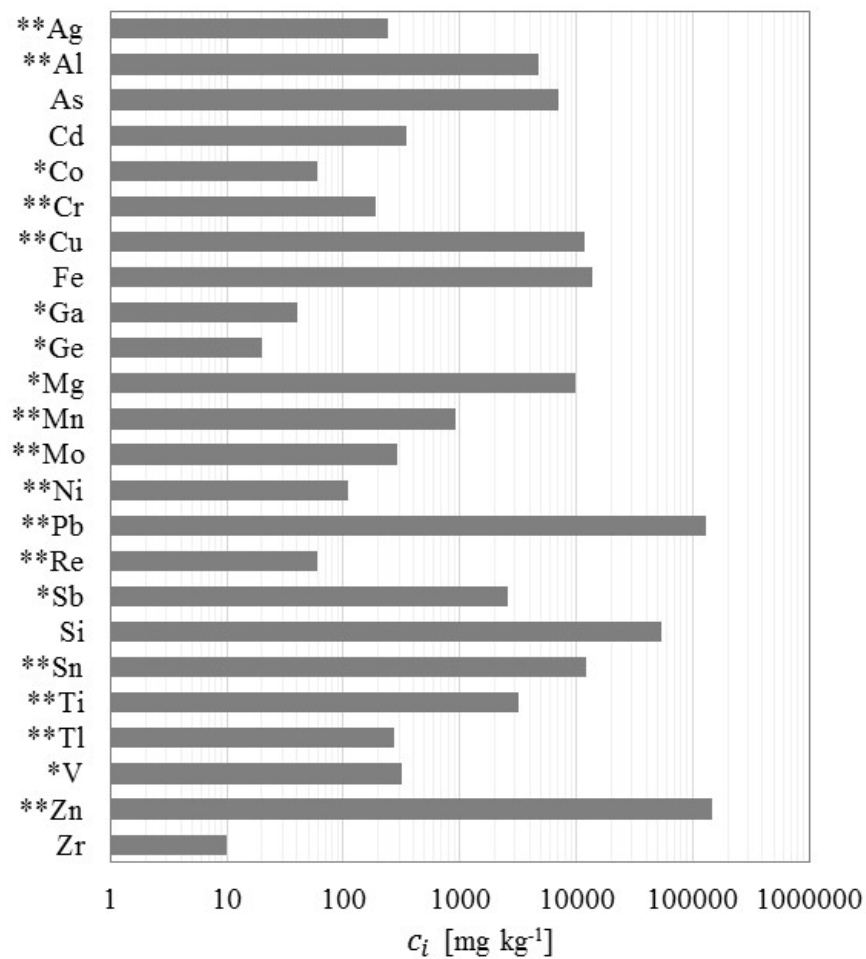


Figure 2.7. Chemical composition of Theisen sludge (*critical and **potentially critical raw material identified by the European Union in 2017) [4,5].

As shown in Figure 2.7, the elements zinc (Zn) and lead (Pb) are the main components in the Theisen sludge. Nevertheless, various elements with a high economic relevance are included, which were classified as critical or potentially critical by the European Union [4,5].

Furthermore, in attending investigations (see Figure 2.5), the metal species of some target elements (e.g. *Ge*, *Mo*, *Re*, *Sb*) were analyzed by the Department of Analytical Chemistry (UFZ, WP8) [34,35]. The results were decisive to interpret the separation behavior of these elements by membranes, adsorption, and solvent extraction. Moreover, the Department of Isotope Biogeochemistry (UFZ, WP10) determined the natural occurring microbiome in Theisen sludge and classified mainly autotrophic microorganisms [36]. The organic content (>10% TOC) in Theisen sludge was analyzed by the Institute of Analytical Chemistry (TU Freiberg, WP9) [36,37].

Parallely to Theisen sludge characterization, the sulfidic bonded elements were mobilized by bioleaching, which was conducted at the TU Bergakademie Freiberg's Institute of Biosciences, Research Group Environmental Microbiology (WP2). Ex situ leaching experiments were performed in 2 L stirred tank bioreactors with 4% Theisen sludge (pulp density) and the leaching bacteria *Acidithiobacillus* and *Acidiphilium*. The temperature was kept constant at 30°C and pH, redox potential, and dissolved oxygen were measured. The obtained leaching solution was acidic (approx. pH 2) and contained a high concentration of *Zn* (3150 mg L⁻¹), *S* (2900 mg L⁻¹), and *Cu* (61.5 mg L⁻¹). Other elements, in contrast, such as *Ge* (0.44 mg L⁻¹) and *Re* (0.39 mg L⁻¹) were only present in traces [38]. The complexity of the bioleaching solution is a great challenge for downstream processing. Therefore, diverse element-specific procedures (see Figure 2.5) shall be connected to a hybrid process for element separation and concentration.

The Institute of Thermal, Environmental and Natural Products Process Engineering (WP7) from Freiberg's University participated with membrane experiments, presented in this work. The aim was to determine the separation behavior and performance of the target elements *Co*, *Cu*, *Ge*, *Mo*, *Re*, and *Zn* by nanofiltration and reverse osmosis (see chapter 3–6). Moreover, microfiltration was tested for Theisen sludge particle and leaching bacteria removal from the leaching solution (see chapter 6).

Another separation approach was the adsorption of anion-forming elements (e.g. *Ge*, *Re*, *Sb*, *V*) from the acidic leaching solution, which was tested by the industrial partner G.E.O.S. Ingenieurgesellschaft mbH (WP3 and 4). First, the adsorption kinetics of the target elements was determined with iron-based adsorbents such as schwertmannite (SHM) in batch experiments. Thereby, the adsorption of *Mo*, *Sb*, and *V* from model single solutions was successfully investigated. Following, small scale column batch experiments were performed with multicomponent model solutions and the real bioleaching solution. The results show that a large amount of *Mo*, *Sb*, and *V* was adsorbed again. An adsorption

of *Re* was feasible with activated carbon. The recovery via desorption was tested with alkalis as *NaOH*, which was effective for *Mo* (100%) and *V* (50%). Moreover, G.E.O.S. investigated the extraction of refractory metals (e.g. *Ag*, *Pb*, *Sn*) from the bioleaching residue. The subsequent leaching was tested in a high-chloride medium using *NaCl*, which was successful for *Pb* (<97%) and *Ag* (<53%). By a conducted alkaline leaching using *NaOH* it is possible to extract *Sn* from the leaching residue [36]. A possible processing chain of Theisen sludge, including the downstream processes adsorption, membrane treatment, and solvent extraction is shown in Figure 2.8.

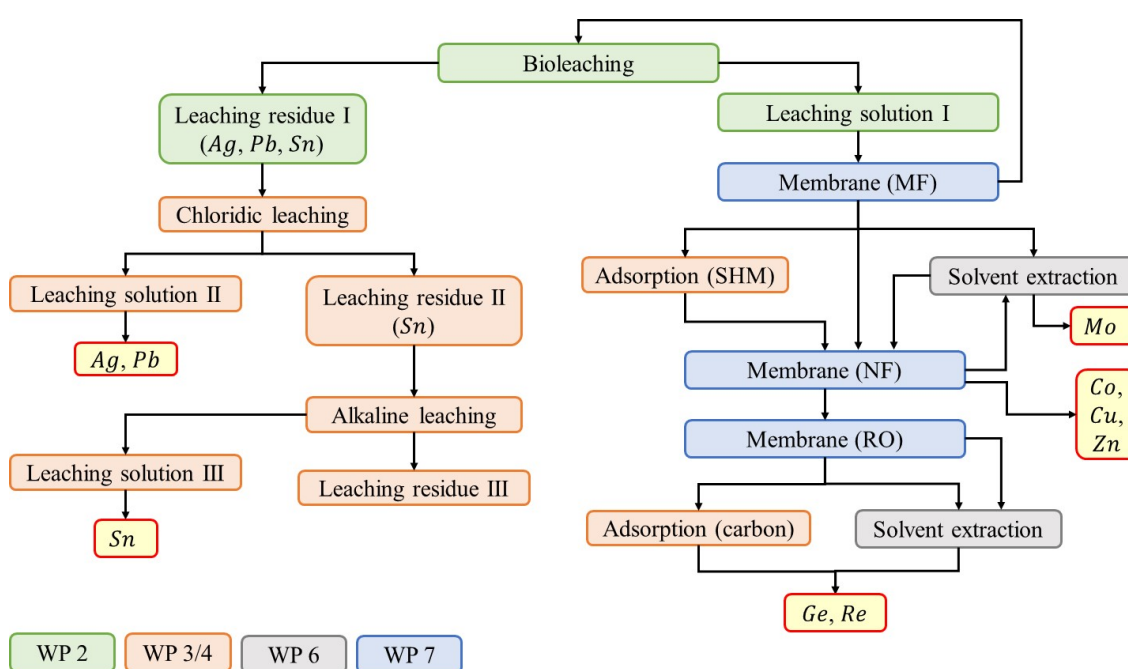


Figure 2.8. Envisioned processing chain of Theisen sludge [36].

Next to membrane techniques and adsorption mechanisms, the solvent extraction was examined as hydrometallurgical process by the Helmholtz Institute Freiberg for Resource Technology (HIF – HZDR, WP6) to separate the target elements (e.g. *Ge*, *Mo*, *Re*) from the aqueous bioleaching solution using organic solvents as Cyanex [39]. pH-dependent batch experiments were conducted with model and the real leaching solution to determine the extraction isotherms and extractions rates. The results show that *Mo* and *Re* can be extracted >97% and *Ge* >77% using several organic solvents [36].

An additional novel approach for element separation was investigated by the BRAIN AG in cooperation with the junior research group BakSolEx (WP5) from TU Bergakademie Freiberg focusing on metallophores, bacterial organic ligands with a low molecular weight, which can complexate metals. The research focused on screening potential metallophores, which can separate the target elements selectively.

After the successful separation and concentration of the valuable elements from the complex acidic bioleaching solution, the concentrates could be refined by e.g. electrolysis. The Nickelhütte Aue GmbH (WP12, see Figure 2.5) would assume the sale and delivery of the produced raffinates. During the project term, this project partner evaluated the market potential of the mono-landfill and the economic efficiency of the developed processing. Currently, the processing costs exceed the market prices of the raffinates [36]. Nevertheless, due to steadily increasing prices of strategic elements globally, the developed approach for Theisen sludge processing could become worthwhile in the future.

In addition to the technical feasibility of the extraction and separation of the strategic elements and an economical consideration, aspects of sustainability and acceptance regarding environmental and social impacts were considered by Adelphi GmbH (WP11, see Figure 2.5) [36].

Thanks to the interdisciplinary cooperation of all project partners, it was possible to develop a concept for the exploration of strategic elements from the mining residue Theisen sludge, including membrane techniques focused in this work.

2.4 Membrane Techniques

Thermal separation processes such as membrane techniques are used in chemical, pharmaceutical, water, and food industry, to name a few. In this work, aqueous solutions are the focus and thus, pressure-driven membrane processes are addressed. These include micro- (MF), ultra- (UF), nanofiltration (NF), and reverse osmosis (RO), which differ in pore diameter as shown in Figure 2.9 [40,41].

d_p	0.1 nm	1 nm	10 nm	100 nm	1 μ m	10 μ m
Water	Monovalent ions	Multivalent ions	Macromolecules	Particle and bacteria		
			Ultrafiltration	Microfiltration		
	Reverse osmosis	Nanofiltration				
<i>TMP</i> [bar]	15–80	10–25	1–10	<2		
<i>TM</i>	Solution-diffusion	Pore-flow solution-diffusion	Pore-flow	Pore-flow		

Figure 2.9. Classification of pressure-driven membrane processes based on pore diameter d_p (*TMP* – transmembrane pressure, *TM* – transport models) [40,41].

The membranes represent a selective barrier between two phases [40] and thus, solutes with a definite size (molecular weight) can be separated from a solution. For particle and bacteria removal MF membranes are applied. Macromolecules such as proteins, lipids, and carbohydrates can be retained by UF membranes. A separation of bivalent (e.g. Mg^{2+} , SO_4^{2-} , Fe^{3+} , PO_4^{3-}) and monovalent (e.g. Na^+ , Cl^-) ions can be realized by NF. With RO membranes it is possible to retain nearly all solutes ($R_i > 99\%$). Due to the fact, that the size of the solutes is decreasing from MF to RO, the transmembrane pressure (TMP) is steadily increasing [40,41]. MF, NF, and RO are described more detailed in the following sections because these membrane techniques are investigated in this work. MF is focused as pre-treatment for particle removal. The separation of the focused elements *Ge* and *Re* shall be realized by NF, and RO is envisioned for concentration.

2.4.1 Microfiltration

The pore diameter of MF membranes typically ranges from 0.1–10 μm [40,41] and thus, between UF and conventional filters [41]. A separation of suspended particles from aqueous solution is feasible by sieving or size exclusion respectively (pore-flow model, see section 2.4.4). During filtration, a low transmembrane pressure (<2 bar) is applied and osmotic pressure is negligible. The industrial applications vary from clarification (beverages) and sterilization (food, pharmaceuticals) to plasmapheresis (medical) and polymeric as well as ceramic membranes ($s = 10\text{--}150 \mu m$) are utilized [40].

The major task of MF is the removal of pathogens and turbidity [42] as well as the concentration of suspensions [43] with partially high solid loadings [44]. Therefore, MF membranes were utilized in this work to investigate retention regarding Theisen sludge particles and leaching bacteria within the leaching solution (see chapter 6). It is envisioned to recycle leaching bacteria for further leaching as shown in Figure 2.8. Afterwards, the clear and sterile solution shall be treated with NF.

2.4.2 Nanofiltration

NF is utilized for processes such as desalination, water softening, and wastewater reclamation. For these purposes, polyamide thin-film composite membranes, manufactured by interfacial polymerization, are frequently utilized, consisting of a sublayer ($s \approx 150 \mu m$) for mechanical resistance and an active surface layer ($s \approx 1 \mu m$) with pores <1 nm [40]. The characteristics and thus, the MWCO of NF membranes ranges between UF and RO [43] and organic (e.g. endocrine disrupting chemicals) [45,46] and

inorganic (e.g. heavy metals) solutes with a molecular weight $\geq 200 \text{ g mol}^{-1}$ can be retained. The peculiarity of NF membranes is the selective separation [43] of monovalent ($R_i < 50\%$) and bivalent ions ($R_i > 90\%$) [40]. The separation is achieved because the membranes have pores (pore flow model) and a dense structure (solution-diffusion model, see section 2.4.4) as well. Moreover, the porous membranes can be charged in dependence of pH of the aqueous solution and thus, the permeation of charged solutes is affected (electrostatic model, see section 2.4.4) [40,41,43,47]. Due to the mentioned characteristics of NF membranes, they seem suitable for the separation of strategic elements, which is investigated in chapter 3–6.

2.4.3 Reverse Osmosis

The structure of RO membranes resembles NF, including a sublayer ($s \approx 150 \text{ }\mu\text{m}$) and an active top layer ($s \approx 1 \text{ }\mu\text{m}$), with a lower degree of opening. Therefore, mono- and bivalent ions are retained at $>98\%$. The separation is based on solution-diffusion and a transmembrane pressure of 15–25 bar for brackish water and 40–80 bar for seawater is applied. The application covers desalination, ultrapure water production, and concentration (food, dairy industry) [40]. Next to NF, RO was examined in this work (see chapter 5–6) for strategic element separation as well as concentration.

2.4.4 Transport Models

In dependence of the membrane's structure (porous, nonporous) and charge, the flux J_i of a solute i through the membrane can be described according to Eq. 6 including convection ($J_{i,c}$), diffusion ($J_{i,d}$), and electromigration ($J_{i,\psi}$). For uncharged solutes, the electromigrative term is omitted [40].

$$J_i = J_{i,c} + J_{i,d} (+J_{i,\psi}) \quad (6)$$

Assuming an ideal solution, the Nernst-Planck equation (see Eq. 7) [40,48] can be applied

$$J_i = K_{i,c} c_i^m J_v - D_i \frac{dc}{dx} - \frac{z_i F c_i^m D_i}{R T} \frac{d\Psi_m}{dx} \quad (7)$$

with the hindered diffusion coefficient D_i , concentration c_i^m within the membrane, valence z_i , and hindrance factor for convection $K_{i,c}$ of a solute i . Ψ_m represents the electric potential difference through the membrane and J_v the volume flux of the permeate. Moreover, the Faraday constant F , gas constant R , and absolute temperature T are

included [40,48]. This equation can be simplified as shown in Eq. 8, involving the proportional coefficient L_i and chemical potential gradient $\frac{d\mu_i}{dx}$ of a solute i [41,49].

$$J_i = -L_i \frac{d\mu_i}{dx} \quad (8)$$

Thereby, the driving force is not restricted to one gradient such as temperature, concentration, pressure or electrical potential because they are interrelated by the chemical potential gradient. Hence, the chemical potential is the overall driving force, which affects the permeant movement because it is interlinked to the flux [41,49].

In an aqueous solution (incompressible phase), the chemical potential μ_i of a solute i is defined according to Eq. 9 [41].

$$\mu_i = \mu_i^0 + RT \ln a_i + \tilde{v}_i (p - p_i^0) \quad (9)$$

where a_i is the activity coefficient and $\tilde{v}_i$ the molar volume of the component i . μ_i^0 is the chemical potential of pure i at a reference pressure p_i^0 and temperature T [41].

Pore-flow Model

The pore-flow model applies for MF and UF and describes the pressure-driven convective flow through the pores of a membrane. Moreover, the model can be applied for NF because the membranes are intermediate between porous and nonporous. The transport of a component, or the separation, respectively, is based on size exclusion (sieving, see Figure 2.10) and thus, on pore size or molecular weight cut-off (MWCO) of the membrane and solute size or rather molecular weight of the solute [40,41].

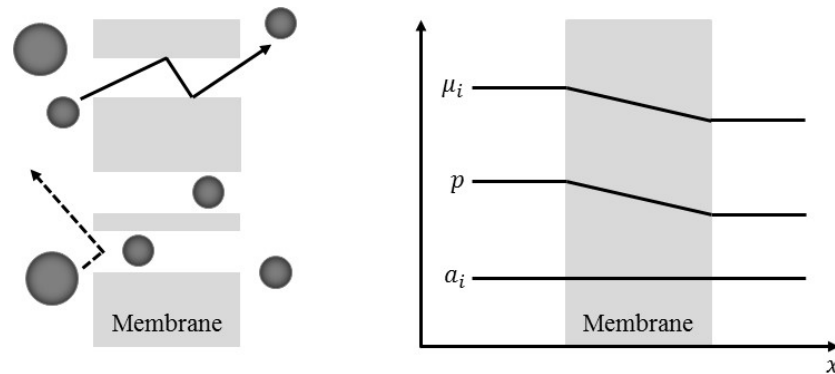


Figure 2.10. Schematic presentation of a pore-flow membrane (μ_i – chemical potential, p – pressure, a_i – permeant activity, x – distance) [41,49]

The pressure gradient across the membrane induces the chemical potential gradient and the permeate concentration is assumed as uniform within the membrane [41]. The pores of the membranes vary in geometry, which has an effect on the transport of the solutes.

Assuming the thickness of the membrane is almost equal to the length of the pores, which have a cylindrical geometry and the same radius r , the flux J_i through the pores can be described by the Hagen-Poiseuille equation (see Eq. 10) [40].

$$J_i = \frac{\varepsilon r^2}{8 \eta \tau} \frac{\Delta P}{\Delta x} \quad (10)$$

As shown in Eq. 10 (ε – surface porosity, τ – pore tortuosity), the viscosity η is inversely proportional to the pressure difference ΔP across the membranes thickness Δx and thus, the flux directly proportional to the applied driving force [40]. By Darcy's law, the flux J_i can be written according to Eq. 11.

$$J_i = K' c_i \frac{dp}{dx} \quad (11)$$

including the pressure gradient $\frac{dp}{dx}$ within the membrane, concentration c_i of component i in the aqueous solution and a coefficient K' , which reflects the nature of the aqueous solution [41].

Solution-diffusion Model

For nonporous or dense membranes (NF, RO), the solution-diffusion model is recommended, assuming that the pressure is uniform within the membrane and the chemical potential gradient is expressed as permeant activity gradient across the membrane, as shown in Figure 2.11 [41,49].

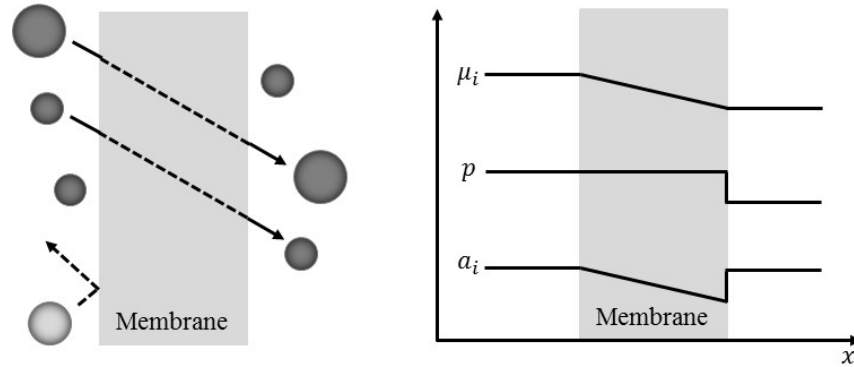


Figure 2.11. Schematic presentation of a solution-diffusion membrane (μ_i – chemical potential, p – pressure, a_i – permeant activity, x – distance) [41,49].

The transport through the membrane is characterized by the permeability, which is a function of solubility (hydrodynamic parameter) and diffusivity (kinetic parameter) from the solute in the membrane [40].

By Fick's first law, stated in Eq. 12, the flux J_i of a solute i can be written as

$$J_i = -D_i \frac{dc_i}{dx} \quad (12)$$

where D_i is the diffusion coefficient and $\frac{dc_i}{dx}$ represents the concentration gradient of component i [40,41,49].

Electrostatic Model

The membrane charge (positive, neutral, negative) is pH-dependent due to the presence of charged groups on the membrane surface and inside the pores. Thus, a separation can be achieved next to the stated convective and diffusive transport by electromigration as shown in Figure 2.12 [40]. Thereby, solutes with the same charge are excluded (Donnan exclusion) but counteracting solutes can permeate freely through the membrane (Donnan effect) if they are not excluded by size [41].

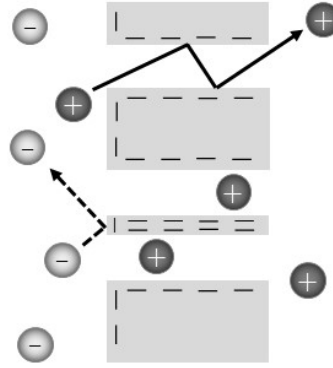


Figure 2.12. Schematic presentation of the electrostatic model of a negatively charged membrane concerning electromigration and dielectric exclusion.

The transport is forced by an electric potential and concentration gradient across the membrane [41]. The built-up Donnan potential Ψ_{don} at the interface between membrane and solution can be calculated according to Eq. 13 [40].

$$\Psi_{don} = \Psi^m - \Psi = \frac{R}{z_i F} T \ln \left(\frac{a_{i,m}}{a_i} \right) \quad (13)$$

If the electrochemical potential E_i of a solute i is equal in the solution (Eq. 14) and in the membrane ($E_{i,m}$, Eq. 15), the Donnan equilibrium (Eq. 16) is established [40,43].

$$E_i = \mu_i + z_i F \Psi = \mu_i^0 + R T \ln a_i + z_i F \Psi \quad (14)$$

$$E_{i,m} = \mu_i^m + z_i F \Psi = \mu_i^{0,m} + R T \ln a_i^m + z_i F \Psi^m \quad (15)$$

$$E_i = E_{i,m} \quad (16)$$

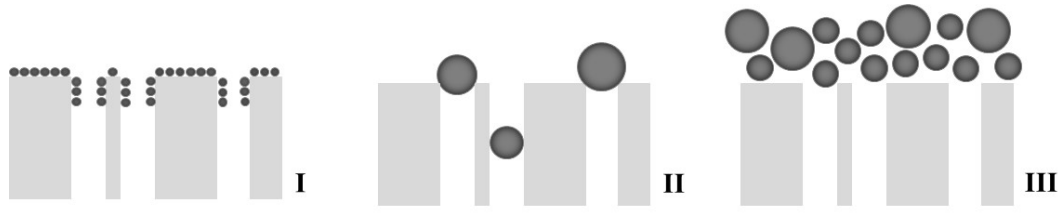


Figure 2.14. Fouling mechanisms (I – scaling/adsorption, II – pore blocking/plugging, III – cake formation) [51].

Scaling is the decomposition of solutes on the membrane surface and inside the pores due to the exceedance of the limit of solubility as consequence of concentration enhancement during filtration [52]. Furthermore, the solute can adsorb on the membrane's surface and within the pores. In both cases, the effective pore size is reduced and thus, the filtration resistance increased and the separation efficiency decreased [43,53]. Scaling and adsorption can occur in all pressure-driven membrane techniques [54].

Particular fouling can cause pore blocking and/or cake formation due to particle decomposition, which are mainly phenomena in MF and UF filtration. Thereby, the insensitivity of fouling depends on membrane and particle nature [51].

Adsorption and particle interaction play a determining role in biofouling evoked by microorganisms, which directly causes a biofilm or fouling by produced substances from their biological activity indirectly [51].

The performance of NF and RO membranes is strongly affected by concentration polarization because the concentration of the retained ionic solutes is strongly enhanced at the membranes surface compared to the bulk solution [41,55]. The build-up concentration profile is shown in Figure 2.15, which induces a diffusive flow back into the bulk [40].

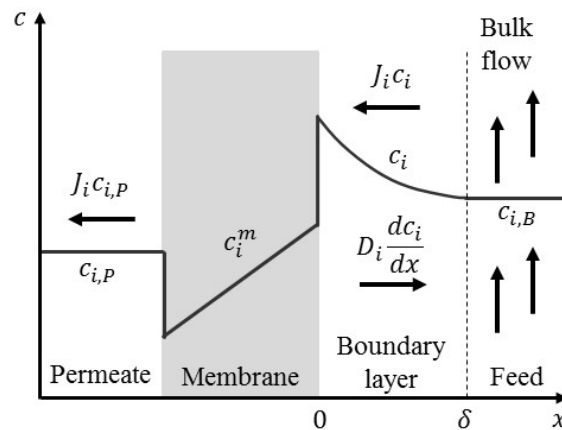


Figure 2.15. Schematic presentation of concentration polarization, illustrated by the concentration profile of a solute i during membrane filtration at steady-state (J – flux, c – concentration, x – distance, δ – thickness) [40,43,56].

If the convective solute flow $J_i c_{i,P}$ is balanced according Eq. 17, steady-state is reached with the following boundary conditions [40].

$$J_i c_i + D_i \frac{dc_i}{dx} = J c_{i,P} \quad (17)$$

$$x = 0 \rightarrow c = c_m$$

$$x = \delta \rightarrow c = c_B$$

An integration of Eq. 17 results in Eq. 18, including the mass transfer coefficient k , shown in Eq. 19, which is the ratio between the diffusion coefficient D_i and the boundary layer thickness δ . The equations illustrate, that the flux J and the mass transfer coefficient k are responsible for concentration polarization [40].

$$\frac{c_i^m - c_{i,P}}{c_{i,B} - c_{i,P}} = \exp\left(\frac{J}{k}\right) \quad (18)$$

$$k = \frac{D_i}{\delta} \quad (19)$$

Different approaches are possible to control and reduce concentration polarization and fouling. First of all, the nature of the feed (e.g. pH, c_i , T , particle size) has a significant influence on boundary layer formation. For example, the pH can be adjusted and thus, the scaling of carbonates can be reduced. Secondly, the membrane nature with parameters such as hydrophilicity, porosity, and zeta potential affect fouling. Furthermore, by controlling the flow velocity (turbulent regime) and generating an enhanced diffusive back flow in the bulk, fouling can be controlled. All in all, the critical flux must not be undercut [56].

2.4.5 Dead-end versus Cross-flow Operation

Two different types of membrane filtration can be distinguished as shown in Figure 2.16. On the one hand, the simplest operation design dead-end, a static filtration with orthogonal feed flow and cross-flow, a dynamic filtration with parallel feed flow on the other hand [40,57,58].

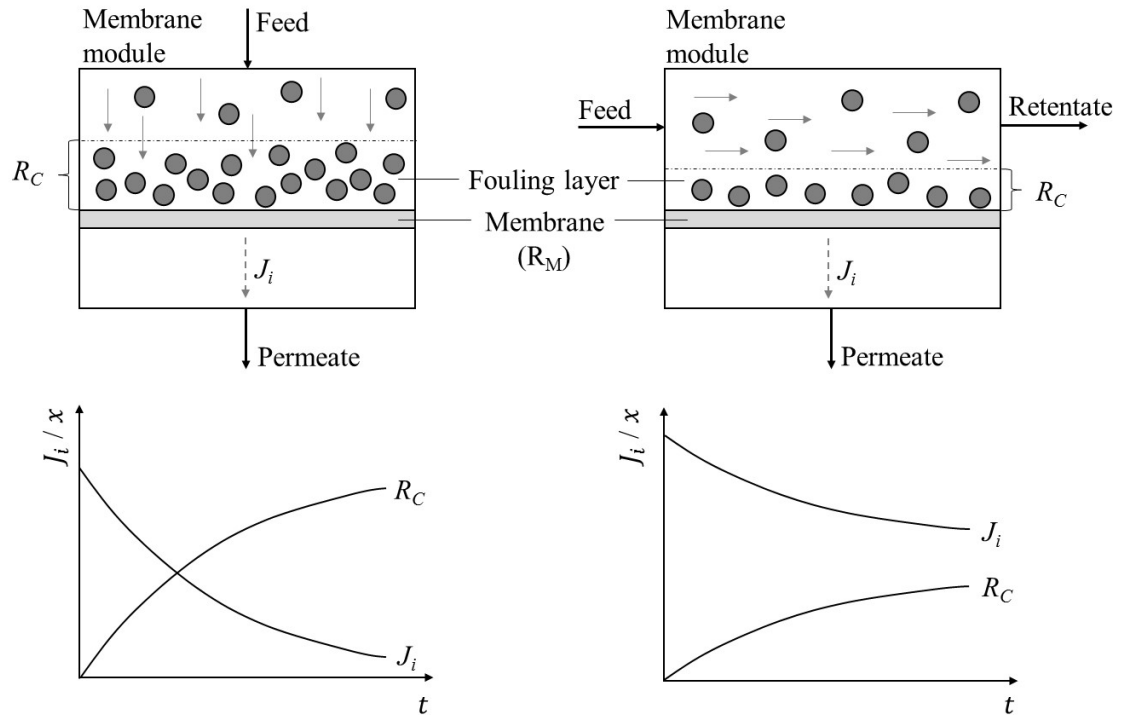


Figure 2.16. Schematic presentation of dead-end (left) versus cross-flow (right) and related flux J_i as well as fouling layer thickness x during operation (t – time, R_C – (cake) layer resistance, R_M – membrane resistance) [40,57,58].

Dead-end represents a discontinuous filtration. Thereby, the feed is forced perpendicularly through the membrane and the concentration of components retained is increasing steadily. As illustrated in Figure 2.16, the flux is decreasing during filtration because the fouling layer is growing with time and thus, the resistance of the layer formation. Fouling can be reduced in cross-flow (continuous filtration) by a tangential flow of the feed across the membrane and flux decline is consequently less pronounced [40,58]. Therefore, cross-flow is preferred for industrial applications due to enhanced membrane efficiency [40]. In dead-end, the filtration performance benefits from the deposit solutes (e.g. particles, microorganisms) because the formed cake layer on the membrane surface represents a secondary filter [58]. Hence, dead-end is frequently utilized for MF applications [40].

3. Influence of pH

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Strategic elements from leaching solutions by nanofiltration – Influence of pH on separation performance

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Abstract

Strategic elements are essential for industrialized countries and both, demand and prices are constantly increasing. The exploitation of so far unutilized polymetallic mining waste could ensure a reliable supply. Mining residues, like the investigated German flue dust deposit from copper ore smelting, represent a promising approach for metal extraction. By bioleaching, the sulfide bonded metals can be dissolved from the mineral phase. Downstream processes are required to separate the target elements from the obtained multicomponent leaching solution. One promising technology is nanofiltration (NF). Three polymeric NF membranes (NF99HF, UTC-60, NP010) were screened to investigate the separation performance of *Co*, *Cu*, *Ge*, *Mo*, *Re*, and *Zn* in a dead-end set-up, in particular the pH-dependent retention. The study shows that pH and thus, the formed ionic species have a major influence on retention and separation performance. Mainly based on size exclusion, a selective separation of *Re* seems feasible with the NF99HF and UTC-60 at pH 7. Under acidic conditions, a separation during concentrating cannot be realized in dead-end by NF because shearing forces and the build-up concentration as well as the electric field gradient forces the permeation of the solutes.

However, if the recovery and ionic strength of the solution is set low, the selectivity can be increased even at pH 2.

3.1 Introduction

The global focus on strategic elements, as raw material for the industry, is significantly increasing since demand has been growing for decades. In the year 2013, the European Commission analyzed 54 raw materials and published a list of 20 critical raw materials (e.g. *Co*, *Ge*, *In*, *W*) with economic importance for the European Union (EU). This crucial evaluation considered the risk of supply, which is associated with e.g. low substitutability, low recycling rates or the dominant supply from few countries only. Approximately 90% of the world's primary supply originates from non-European countries, headed by China [1]. To remain competitive and assure long-term growth of the economy, the EU is constantly investigating reliable access routes to raw and critical raw materials [2]. Therefore, sustainable and unexploited resources need to be tapped and extraction processes shall be developed to exploit currently non-utilizable complex ore deposits [3]. Numerous mineral mining dumps represent an unexploited resource potential for strategic elements. In the present study, a deposited flue dust from German copper ore smelting, the so-called Theisenschlamm (Theisen sludge), represents the feedstock for a proposed hybrid process, which shall include bioleaching and downstream processes like nanofiltration.

3.1.1 Theisen sludge

The feedstock of interest is a waste by-product from the industrial copper extraction of a bituminous Permian black marine shale, the so-called Kupferschiefer. The shale was mined for 800 years in the Mansfeld district (Saxony-Anhalt, Central Germany) [4–6]. In a blast furnace, the Kupferschiefer was smelted at approx. 1300°C and accrued flue dust from top gas scrubbing was suspended in water in a Theisen-scrubber, which was invented 1904 and named after its inventor. The resulting slurry had a solid content of 3 g L⁻¹ and was dewatered to about 60 g L⁻¹. The remaining fine-grained scrubber dust slurry was utilized until 1978 as raw material for lead, zinc, and germanium production. After the German reunification, the copper extraction became unprofitable and was halted in 1990. By then, more than 220000 t of Theisen sludge were deposited in open ponds and basins, which remain unsealed to the ground and surface [6–10]. Beginning 2001, the residues were restored at a mono-landfill site called Teich 10 (Pond 10), which is located

in Helbra (Saxony-Anhalt) in Germany. In 2006, a surface sealing was installed and end of pipe treatments are required to this day [6,9,11]. However, the stored material still represents a threat to the environment as well as a potential industrial feedstock [6–10]. The composition of the Theisen sludge is shown in Table 3.1

Table 3.1. Literature review of the composition of Theisen sludge in comparison to the detected element concentration in the sampled sludge.

Ele- ment	c_i [mg kg ⁻¹]							Sampled sludge
	Literature review							
	1992 ^{a)} 1994 ^{b)}	†1996 ^{c)}	1997 ^{d)}	1998 ^{e)}	2004 ^{f)}	†2015 ^{g)}	2016 ^{h)}	
<i>Ag</i> **	430	320	240	520	350	n. a.	430	240
<i>Al</i> **	n. a.	n. a.	4700	23600	9400	14100	11000	4700
<i>As</i>	6500	5800	7000	4100	6300	7600	9100	7000
<i>Cd</i>	400	790	350	360	380	400	290	350
<i>Co</i> *	n. a.	n. a.	60	80	n. a.	n. a.	130	60
<i>Cr</i> *	n. a.	n. a.	190	890	110	n. a.	n. a.	190
<i>Cu</i> **	12000	12000	11700	14100	12300	16000	12100	11700
<i>Fe</i> **	n. a.	n. a.	13600	30900	15200	17000	15000	13600
<i>Ga</i> *	n. a.	n. a.	40	80	n. a.	n. a.	n. a.	40
<i>Ge</i> *	60	n. a.	20	30	n. a.	n. a.	20	20
<i>Mg</i> *	n. a.	n. a.	9800	2500	2500	2600	n. a.	9800
<i>Mn</i> **	n. a.	n. a.	920	670	740	340	640	920
<i>Mo</i> **	700	420	290	600	480	520	350	290
<i>Ni</i> **	100	n. a.	110	510	490	80	n. a.	110
<i>Pb</i>	140000	121000	132000	122000	81300	134000	97900	132000
<i>Re</i> **	100	n. a.	60	60	n. a.	30	90	60
<i>S</i>	160000	n. a.	83100	113000	151000	155000	121600	83100
<i>Sb</i> *	4500	3900	2600	1500	4900	3200	2100	2600
<i>Si</i>	n. a.	n. a.	54100	n. a.	100000	75000	n. a.	54100
<i>Sn</i> **	12000	14000	12100	17200	n. a.	14100	n. a.	12100
<i>Ti</i> **	n. a.	n. a.	3200	5000	700	n. a.	n. a.	3200
<i>Tl</i> **	230	310	270	320	n. a.	n. a.	n. a.	270
<i>V</i> **	n. a.	n. a.	320	n. a.	n. a.	n. a.	n. a.	320
<i>Zn</i> **	180000	139000	149000	163000	241000	184000	250400	149000
<i>Zr</i>	n. a.	n. a.	10	970	n. a.	n. a.	n. a.	10

*critical raw material [1], **candidate critical raw materials [1], †literature data in %, n. a. – not available

^{a,b)}[6–8,10], ^{c)}[9,12], ^{d)}[6], ^{e)}[13], ^{f)}[14], ^{g)}[15], ^{h)}[16]

The metals lead and zinc are predominant in the Theisen sludge (see Table 3.1) with more than 10% (w/w) each. Moreover, a high amount of sulfur is included due to the fact that the particles have a similar crystal structure to sphalerite (*ZnS*), wurzite (β -*ZnS*), and

galena (PbS) [6]. Besides, the sludge contains highly toxic elements such as arsenic and cadmium. However, significant amounts of critical raw materials (e.g. Co , Ge , Sb) and candidate raw materials (e.g. Al , Mo , Re) are included. The elements are not homogeneously distributed in the Theisen sludge matrix. Hence, reported compositions and the amount of detected elements may deviate from each other because samples were taken from different points of withdrawal.

Since 1978, various pyro- and hydrometallurgical concepts have been applied to extract valuable elements from the Theisen sludge but until now, an economically feasible process is lacking [6,8,17]. By bioleaching and subsequent downstream processes, the access to untapped strategic elements shall be implemented.

3.1.2 Bioleaching

The intended microbial leaching process is a simple, eco-friendly, and effective technique to extract metals from low-grade ores and is conducted under acidic conditions (pH 1.5–3) [18–20]. The major amount of the metals in Theisen sludge consists of amorphous sulfide particles [6,21] and thus, bioleaching should be amenable [16]. The metals can be solubilized from the mineral phase directly by the metabolism of leaching bacteria or indirectly by the products of the bacteria metabolism [18,22,23]. Acidophilic microorganisms like *Acidithiobacillus* and *Thiobacillus* are the most active species involved in bioleaching. After solubilization, the majority of metals remain as ions in the solution [18–20,22,24,25]. Klink et al. (2016) investigated the bioleaching potential of Theisen sludge with *Acidithiobacillus ferrooxidans* in shaking flasks and 2 L stirred-tank bioreactors for 25 d at 30°C [16]. The performed bioleaching demonstrates that valuable strategic elements can be solubilized from Theisen sludge (see Table 3.2) but further process optimization is required to increase the extraction yield [16,26].

Table 3.2. Composition (selected elements) of the bioleaching solutions of Theisen sludge [16,26].

Experimental set-up	c_i [mg L ⁻¹]							
	Zn^{**}	S	Fe^{**}	Cu^{**}	Co^*	Ge^*	Re^{**}	Mo^{**}
Shaking flask (1% solid load)	1640	1950	226	53.5	0.52	0.26	0.21	<0.06
Bioreactor (4% solid load)	3150	2900	50	62	0.99	0.44	0.39	0.02

*critical raw material [1], **candidate critical raw materials [1]

The mobilized elements need to be separated and concentrated from the complex multicomponent leaching solution with a wide range of concentration (see Table 3.2) by element-specific procedures like solvent extraction, anion exchange, and membrane technology, which shall be linked together in a hybrid process [27]. The present paper investigates the applicability of nanofiltration.

3.1.3 Nanofiltration

Nanofiltration (NF) is a pressure-driven (10–25 bar) membrane process and the application enables the separation of uncharged solutes, monovalent (e.g. Na^+ , Cl^- <50%) and multivalent (e.g. Mg^{2+} , SO_4^{2-} >90%) ions. The majority of NF membranes consist of chemically stable polymers. Asymmetric thin-film composite membranes with a dense active surface layer (thickness $\leq 1 \mu m$) and a porous support layer (thickness: 50–150 μm) are frequently utilized [28].

For NF membranes, the size exclusion and solution-diffusion model are applicable because the membrane properties lie between ultrafiltration (UF) and reverse osmosis (RO) membranes [29]. The basic separation mechanism of porous membranes (UF) is size exclusion, which is forced by a pressure gradient. Particles or molecules, which are larger than the pore size, were retained [28,20]. For nanofiltration membranes, Mulder (1996) indicates a pore size below 2 nm [28] and solutes with a molecular weight above 200 Da can be retained [31]. For non-porous membranes (RO), the solution-diffusion transport model is widely used. The diffusion of the solutes is forced by a chemical potential gradient over the membrane [28,30,32].

Furthermore, in dependence of the isoelectric point, which is influenced by e.g. pH and ionic strength of the solution, the membrane charge can be negative, neutral or positive [30,33,34]. Related charge interactions between charged membrane and charged solute can refer to attraction or repulsion (dielectric exclusion) [29,30,33]. Moreover, adsorption processes between solute and membrane can affect the mass transport across the membrane. In the majority of cases, the different mechanisms apply concurrently [28,30].

In the present study, the pH-dependent separation performance of the strategic elements *Co*, *Cu*, *Ge*, *Mo*, *Re*, and *Zn* was investigated. The experiments were performed in dead-end set-up with three polymeric nanofiltration membranes (NF99HF, UTC-60, NP010). The study aimed at investigating the basic separation mechanisms and optimal process conditions for the given separation task.

3.2 Materials and Methods

3.2.1 Synthetic Feed Solutions

In reference to the bioleaching solution of Theisen sludge (see Table 3.2) and for adequate handling, different synthetic feed solutions were prepared to investigate the pH-dependent separation performance of the focused strategic elements because literature data, especially for *Ge*, *Mo*, and *Re*, are barely or non-existent. The experimental design is shown in Table 3.3. Currently, experiments cannot be conducted with real leaching solutions because the generated volumes are too low for NF experiments. Nevertheless, a pretreatment (micro- and ultrafiltration) is required to remove suspended particles and bacteria to avoid fouling in the intended NF process.

Table 3.3. Experimental design for the dead-end set-up (TMP: 15 bar, T: 25°C, N: 500 rpm, pH: 2, 4, and 7, recovery: 50%).

Feed composition [Element]	$c_{i,F}$ [mg L ⁻¹]	Membrane		
		NF99HF	UTC-60	NP010
<i>Ge</i> <i>Mo</i> <i>Re</i>	1.0 0.5 1.0	✓	✓	✓
<i>Ge</i> <i>Mo</i> <i>Re</i> <i>Co</i>	1.0 0.5 1.0 2.0	✓	✓	✓
<i>Ge</i> <i>Mo</i> <i>Re</i> <i>Co</i> <i>Cu</i>	1.0 0.5 1.0 2.0 10	✓	✓	✗
<i>Ge</i> <i>Mo</i> <i>Re</i> <i>Co</i> <i>Cu</i> <i>Zn</i>	1.0 0.5 1.0 2.0 10 10	✓	✓	✗
	1.0 0.5 1.0 2.0 10 10	✓	✓	✗
	recovery: 10%	(pH 2)	(pH 2)	✗

First, the anion forming elements (*Ge*, *Mo*, *Re*) were combined and in addition, the cations *Co*, *Cu*, and *Zn* were added successively to the synthetic feed solution. The concentration of *Cu* and *Zn* is not referred to the leaching solution as the scope was to examine the principal influence of these main components on the separation performance. Side effects, which might be evoked by significantly increased ionic strength, should be excluded. Following this, the influence of the recovery was evaluated (see Table 3.3).

The experiments were conducted at pH 2 and 4 because the final pH of the real leaching solution is acidic and below pH 4 and typically in the range of pH 2 [16]. Furthermore, pH 7 was chosen to determine the influence of changing ionic species and membrane surface charge on the separation performance. All experiments were conducted in double determination. The respective feed solution was prepared by adding the required amount of the chemical compound (see Table 3.4) to deionized water.

Table 3.4. Chemical compounds used for the synthetic feed solutions.

Element	Chemical compound	Empirical formula	Purity [%]	Manufacturer
<i>Co</i>	Cobalt(II) sulfate heptahydrate	$CoSO_4 \cdot 7H_2O$	99+	AnalaR Normapur
<i>Cu</i>	Copper(II) sulfate	$CuSO_4$	≥ 99.0	Sigma Aldrich
<i>Ge</i>	Germanium(IV) dioxide	GeO_2	99.999	Alfa Aesar
<i>Mo</i>	Sodium molybdate(VI) dihydrate	$Na_2MoO_4 \cdot 2H_2O$	98.0	Alfa Aesar
<i>Re</i>	Sodium perrhenate(VII)	$NaReO_4$	99+	Alfa Aesar
<i>Zn</i>	Zinc(II) sulfate monohydrate	$ZnSO_4 \cdot H_2O$	≥ 99.0	Sigma Aldrich

The pH of the feed solutions was adjusted with $NaOH$ (0.1 M) or H_2SO_4 (1 M). The feed concentration was verified with ICP-MS (Agilent Technologies Inc., 7700 Series: *Co*, *Ge*, *Mo*, *Re*) and ICP-AES (Spectro Analytical Instruments GmbH, Ciros: *Cu*, *Zn*).

3.2.2 Experimental Set-up

By means of dead-end experiments, the pH-dependent retention of *Co*, *Cu*, *Ge*, *Mo*, *Re*, and *Zn* during concentrating was investigated. Experiments were performed in a batch cell (Andreas Junghans GmbH & Co. KG, $V_{max} = 350$ mL, $p_{max} = 20$ bar) and the schematic set-up is illustrated in Figure 3.1.

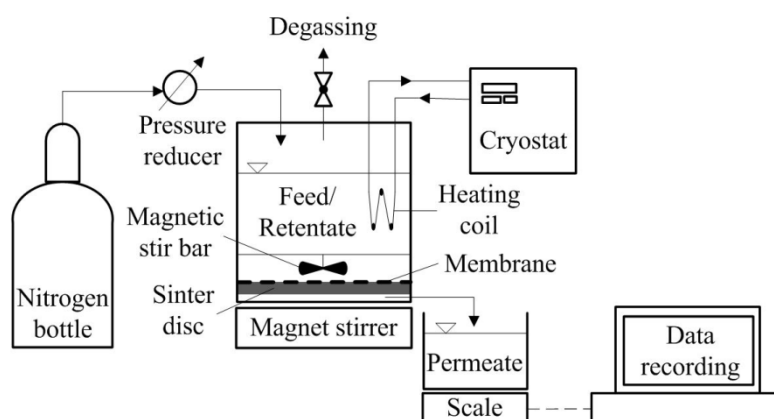


Figure 3.1. Schematic presentation of the dead-end set-up.

The utilized membrane had an active surface area of 40 cm² and was installed in the bottom of the batch cell upon a sinter disc, which provides mechanical resistance (see Figure 3.1). In advance, the virgin membrane was conditioned with Ultrasil® (15 g L⁻¹) for 45 min. For each experiment, 300 mL feed was filled in the batch cell. Subsequently, the batch cell was impinged with nitrogen. The required pressure of 15 bar was built up by a pressure reducer. During the experiment, the pressure and temperature (25°C) was

kept constant and the feed/retentate was homogenized with a magnet stirrer (N : 500 rpm). The permeate was filtered through the membrane and was led out pressureless. Received permeate was weighted on a precision scale (Kern & Sohn GmbH, Typ PCB 2500, readout: 0.01 g). By achieving a recovery of 50% (see Eq. 1), the experiment was terminated.

$$Recovery = \frac{m_{P,t=end}}{m_{F,t=0}} \cdot 100\% \quad (1)$$

Between each experiment, the membrane was flushed with 150 mL deionized water. The membrane was substituted by a new flat-sheet after a test serial of six attempts. To evaluate the separation performance of the utilized membranes, the retention R_i was calculated by comparing the concentration of an element c_i in the permeate ($c_{i,P}$) to those in the retentate ($c_{i,R}$) according to Eq. 2. In consequence of dynamic retentate concentrating, the feed concentration cannot be used as reference.

$$R_i = \left(1 - \frac{c_{i,P}}{c_{i,R}}\right) \cdot 100\% \quad (2)$$

The *Ge*, *Re*, *Mo*, and *Co* concentration was measured with ICP-MS (Agilent Technologies Inc., 7700 Series). The *Cu* and *Zn* concentration was analyzed using an ICP-AES (Spectro Analytical Instruments GmbH, Ciros) because of the expected higher concentration.

3.2.3 Nanofiltration Membranes

Three commercially manufactured nanofiltration membranes (NF99HF, UTC-60, NP010) were identified as suitable for the proposed separation task (see Table 3.5). The membranes were chosen due to their high permeability, chemical resistance, and on the basis of previous investigations [35–38]. However, for the NF99HF and UTC-60 the manufacturer recommends a pH range between 3 and 10. Hence, long time experiments are required because the separation performance was additionally evaluated at pH 2. Nevertheless, during the experiments a damage, especially of the active layer, could not be observed.

Table 3.5. Characteristics of the utilized nanofiltration membranes. Unmarked information was provided by the manufacturer.

Characteristic	Membrane		
	NF99HF	UTC-60	NP010
Manufacturer	Alfa Laval AB (Sweden)	Toray Ind. Inc. (Japan)	Microdyn-Nadir GmbH (Germany)
Nomenclature	Thin-film composite	Thin-film composite	Flat sheet
Active layer	Polyamide	Poly(piperazine)amide	Polyethersulfone
Support layer	Polysulfone	Polysulfone	Polyethylene/Polypropylene
Support paper	Polyester	Polyester	–
MWCO [Da]	200	150–300	1000
T_{max} [°C]	50	45	95
p_{max} [bar]	55	41	40
pH range	3–10	3–8	0–14
IEP [pH]	4.1–4.4 ^{a)}	3.2 ^{c)}	3 ^{g)} –4 ^{h)}
R_i [%]	<i>NaCl</i> 72 ^{b)}	<i>NaCl</i> 30 ^{d)} –55	<i>NaCl</i> 10
	<i>Na₂SO₄</i> 97 ^{b)}	<i>Na₂SO₄</i> 76 ^{d)}	<i>Na₂SO₄</i> 35–75
	<i>MgSO₄</i> ≥98	<i>MgSO₄</i> ≥97	<i>MgSO₄</i> 25–55 ^{b)}
L_p^* [kg m ⁻² h ⁻¹ bar ⁻¹]	9–18 ^{b)}	10 ^{e)} –15 ^{f)}	11–30 ^{b)}

*pure water

^{a)}[39], ^{b)}[40], ^{c)}[41], ^{d)}[42], ^{e)}[43], ^{f)}[44] ^{g)}[45,46] ^{h)}[45,47]

As shown Table 3.5, the NP010 has the highest MWCO. Therefore, the retention of *NaCl*, *Na₂SO₄*, and *MgSO₄* is expected to be reduced. Nonetheless, the pure water permeability of all membranes is almost equal. Moreover, the polymeric membranes carry a pH-dependent surface charge. At the isoelectric point, usually between pH 3–6, the membranes are electrically neutral, below positively, and above negatively charged. Charge interactions with charged solutes can refer to attraction or repulsion [30,33,34,48]. However, basic information about the main separation mechanisms of the target strategic elements is non-existent and thus, the pH-dependent separation performance was investigated in dead-end set-up.

3.3 Results and Discussion

3.3.1 Ternary Experiments with *Ge*, *Mo*, and *Re*

The utilized feed solution contained the anion forming elements *Ge* (1.0 mg L⁻¹), *Mo* (0.5 mg L⁻¹), and *Re* (1.0 mg L⁻¹) in combination. The dead-end experiments were conducted at pH 2, 4, and 7 to investigate the influence of the ionic species and membrane surface charge on the separation performance (see Figure 3.2).

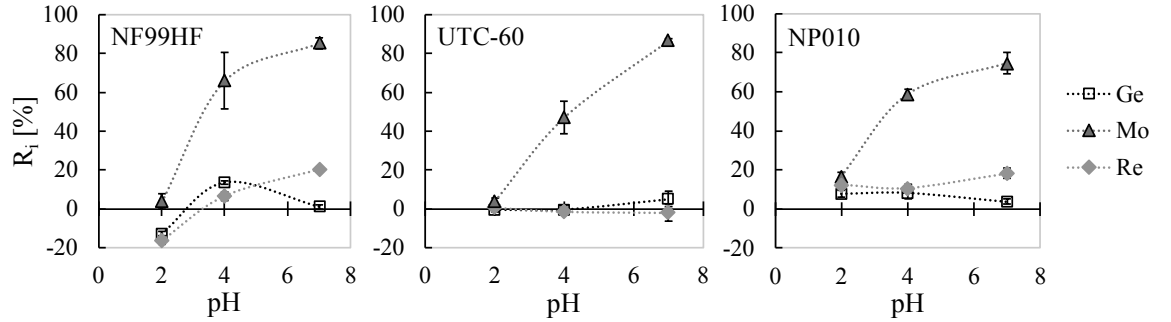


Figure 3.2. pH-dependent retention R_i of the combined elements *Ge*, *Mo*, and *Re* in dead-end set-up (TMP: 15 bar, T: 25°C, N: 500 rpm) for the NF99HF, UTC-60, and NP010.

pH-dependent *Ge* Retention

As shown in Figure 3.2, the germanium retention is very low for all tested membranes ($\leq 18\%$). In the investigated pH range, the predominant species is $Ge(OH)_4^0$ (germanic acid) [49,50]. Therefore, charge interactions with the membrane surface can be excluded. In that case, the convective hindrance factor $K_{i,c}$ can be calculated according to Eq. 3 [51,52].

$$K_{i,c} = (2 - \Phi)(1 + 0,054\lambda - 0,988\lambda^2 + 0,441\lambda^3) \quad (3)$$

The factor $K_{i,c}$ is a function of λ , which is the ratio between the radius of the solute r_s and the pore radius r_p . The steric partitioning coefficient Φ can be estimated according to Eq. 4 [51,52].

$$\Phi = (1 - \lambda)^2 = \left(1 - \frac{r_s}{r_p}\right)^2 \quad (4)$$

Under consideration of $K_{i,c}$ and Φ , the limiting retention $R_{i,lim}$ can be determined after Eq. 5 for the uncharged solutes [52].

$$R_{i,lim} = 1 - K_{i,c}\Phi \quad (5)$$

Alternatively, the reflection coefficient σ can be calculated according to Eq. 6 [53,54].

$$\sigma = 1 - \left(1 + \frac{16r_s^2}{9r_p^2}\right) \left(1 - \frac{r_s}{r_p}\right)^2 \left[2 - \left(1 - \frac{r_s}{r_p}\right)^2\right] \quad (6)$$

Oatley et al. (2012) indicated a pore radius of 0.430 nm for the NF99HF [39]. Data about the UTC-60 are non-existent but the MWCO (150–300 Da) indicates that the pore radius is in the same range as the NF99HF (200 Da). For the NP010 (1000 Da), a pore radius of 0.745 nm is reported in the literature [55]. The radius of uncharged solutes r_s can be calculated according to Eq. 7. The given empirical correlation is valid for molecules with a molecular weight (MW) to 600 g mol⁻¹ [56].

$$r_s = \frac{0.065 \cdot MW^{0.438}}{2} \quad (7)$$

The calculated radius of germanic acid (MW = 140.67 g mol⁻¹) is 0.284 nm. However, the solute radius seems overestimated as the mean distance of the *Ge-O* bond is reported between 173.8 and 175 Å [50,57,58]. In the literature, the length of an *O-H* bond is reported with 1.1 Å [59] and thus, the radius of $Ge(OH)_4^0$ can be approximated with 0.185 nm. By using the open source web-application MolView [60], the distance of the *Ge-O* bond was estimated with 184 Å, which corresponds with the literature data. The distance of opposing *-OH* bonds was determined with 0.412 nm and thus, the radius $Ge(OH)_4^0$ is approximately 0.206 nm. For this reason, a size exclusion can be almost disregarded. Nevertheless, the small amount of retention observed (see Figure 3.2) is the result of size exclusion due to the presence of pore size distribution. The calculated limiting retentions and reflection coefficients of $Ge(OH)_4^0$ are shown in Table 3.6 for the NF99HF and NP010.

Table 3.6. Convective hindrance factor, steric partitioning coefficient, and the limiting retention as well as the reflection coefficient of $Ge(OH)_4^0$ with a radius between 0.185–0.206 nm for the NF99HF and NP010.

Membrane	$K_{i,c}$ [–]	Φ [–]	$R_{i,lim}$ [%]	σ [%]
NF99HF	1.46–1.47	0.27–0.32	52.4–60.2	27.7–34.0
NP010	1.38–1.40	0.52–0.57	22.2–26.7	10.0–12.2

As shown in Table 3.6, the convective hindrance factor is slightly increased for the NF99HF due to the smaller MWCO. Therefore, the limiting retention as well as the reflection coefficient of $Ge(OH)_4^0$ is enhanced compared to the NP010. The estimated reflection coefficient σ is closer to the experimental data but, the determined *Ge* retention is much lower for the NF99HF as predicted (see Figure 3.2). It has to be considered that

the shown values are predictions for the uncharged germanic acid in a single element solution. Mutual interactions as consequence of combination were not considered. However, the estimated retention cannot be achieved as the build-up concentration gradient during filtration as well as the flow direction forces the permeation of the solutes. Tansel et al. (2006) reported that ions can permeate through the membrane pores even if their hydration radius is larger than the pore radius because hydration water can be lost as consequence of a high shear force in flow direction. Therefore, the ion permeability is enhanced in dead-end [61]. It can be assumed that changed hydrodynamic conditions in cross-flow lead to increased retentions, which are closer to the estimated values because the shearing forces are reduced.

pH-dependent Mo Retention

The experiments were performed with a total molybdenum concentration of 0.5 mg L^{-1} , which compiles 0.005 mM . The *Mo* species distribution diagram for a molybdate concentration of 0.03 mM is shown in Figure 3.3 because the ionic species varies in dependence of concentration and pH.

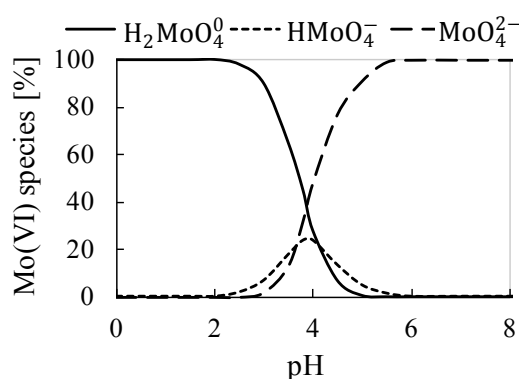


Figure 3.3. Species distribution diagram of Mo(VI) in aqueous solution as function of pH with a total molybdate concentration of 0.03 mM [62].

As shown in Figure 3.3, the neutral species $H_2MoO_4^0$ (molybdic acid) is present in aqueous solution at pH 2. According to Eq. 7, the radius of the uncharged molybdic acid ($MW = 161.95 \text{ g mol}^{-1}$) is 0.302 nm , which seems overestimated again. Literature data about the solute radius are not available. In consideration of the dissymmetric steric formation of $H_2MoO_4^0$ [60], the molecular extension varies between 0.169 nm (width) and 0.247 nm (length). In Table 3.7 the limiting retentions as well as the reflection coefficients of $H_2MoO_4^0$ are shown for the NF99HF and NP010.

Table 3.7. Convective hindrance factor, steric partitioning coefficient, and the limiting retention as well as the reflection coefficient of $H_2MoO_4^0$ with a radius between 0.169–0.247 nm for the NF99HF and NP010.

Membrane	$K_{i,c}$ [–]	Φ [–]	$R_{i,lim}$ [%]	σ [%]
NF99HF	1.43–1.46	0.18–0.37	46.2–74.0	23.4–47.7
NP010	1.36–1.44	0.45–0.60	19.0–35.8	8.5–17.0

In comparison to germanic acid, the steric hindrance of molybdic acid should be enhanced due to the enlarged solute radius. Therefore, the estimated limiting retention, respectively the reflection coefficient is increased. Once again, the estimated retention of the NP010 corresponds with the experimental data (pH 2 $\leq$ 19%). This cannot be observed for the NF99HF (pH 2 $\leq$ 9%), which shows much lower retentions than predicted. Similar to germanium, the permeation of molybdenum is forced by the build-up concentration gradient and flow direction. This effect seems connected with the pore radius of the membrane and is more pronounced for the NF99HF because the shearing forces in flow directions are enhanced. Moreover, the diffusion is enhanced if the pore radius becomes smaller [63].

However, with increasing pH, the *Mo* species $HMoO_4^-$ and MoO_4^{2-} are formed and MoO_4^{2-} is dominated above pH 6 (see Figure 3.3) [62]. The presence of the varying *Mo* species in dependence of pH has a considerable impact on the retention as shown in Figure 3.2. The retention increased up to 47–66% at pH 4 because the formed anions are repulsed. In presence of MoO_4^{2-} , the retention is further enhanced and achieves 75–87% at pH 7. Next to dielectric exclusion, the formed anions are additionally rejected by size. In general, the hydrated radius of divalent anions is more extensive compared to monovalent ones and thus, the divalent MoO_4^{2-} (0.385 nm [64]) is subject to greater size exclusion.

pH-dependent Re Retention

Similar to germanium, rhenium shows low retentions in the investigated pH-range. Rhenium is present as ReO_4^- (perrhenate) [65] with a hydrated radius of 0.260 nm [66]. The permeation is supported because size exclusion seems negligible. Moreover, it is conceivable that ReO_4^- is attracted by the positively charged membrane surface at pH 2. Due to a more positively charged membrane surface of the NF99HF, the lower *Re* retention in comparison to the UTC-60 and NP010 could be explained. Above the IEP, polyamide membranes are acidic, dissociated, and composed of carboxylic groups

($-COO^-$) [67]. Therefore, repulsion leads to an enhanced retention at pH 7. The *Re* repulsion was observed for the NF99HF ($\leq 22\%$) and NP010 ($\leq 21\%$) but not for the UTC-60 ($\leq 2\%$).

Mutual Interactions

The permeation of charged solutes is forced by an electrochemical potential difference ($\Delta\mu_i \neq 0$) between the feed (respectively retentate) and permeate because the chemical potential ($RT\ln C_i$) and electrical potential ($z_i F\varphi$) differ in the bulk solutions. Assuming simplified conditions, the electrochemical potential μ_i can be expressed according to Eq. 8 for each ion i [28,68–70]. The swelling pressure, which originates from the shrunken polymeric matrix, was excluded since the influence on the ionic distribution can be neglected [28].

$$\mu_i = \mu_i^o + RT\ln C_i + z_i F\varphi \quad (8)$$

Next to the standard chemical potential μ_i^o , the equation contains the gas constant R , the absolute temperature T , the valence z_i of the ion i , and the Faraday constant F . For dilute solutions, the concentration C_i is admissible. In case of concentrated solutions, the activity a_i is used instead. The standard potential μ_i^o shall be equal for both bulk solutions. Therefore, the potential difference $\Delta\varphi$ between the bulk solutions was estimated after Eq. 9 [28,68–70].

$$\Delta\varphi = \frac{RT}{z_i F} \cdot \ln \frac{C_{i,R}}{C_{i,P}} \quad (9)$$

The given Nernst equation describes the electrical force, which can transport an ion against its concentration gradient and thus, the retention can also become negative. This can be clearly observed for the NF99HF at pH 2 (see Figure 3.2). As a consequence, the potential difference $\Delta\varphi$ becomes positive as shown in Table 3.8.

Table 3.8. Potential difference $\Delta\varphi$ of the charged solutes between the bulk solutions for the ternary experiments.

pH	Ionic species	$\Delta\varphi$ [mV]		
		NF99HF	UTC-60	NP010
2	ReO_4^-	3.9	-0.2	-3.4
	ReO_4^-	-1.7	0.4	-2.9
4	$HMoO_4^-$	-7.2	-4.3	-5.9
	MoO_4^{2-}	-6.9	-4.1	-5.7
7	ReO_4^-	-5.8	0.5	-5.2
	MoO_4^{2-}	-24.6	-26.0	-17.6

The potential difference of ReO_4^- becomes slightly negative at pH 4 for the NF99HF and NP010, which indicates repulsion. As shown in Table 3.8., the charge interactions are more pronounced at pH 7 due to the more negatively charged membrane surface. Therefore, the potential difference is lower compared to pH 4. This effect is enhanced for MoO_4^{2-} and thus, the potential difference at pH 7 significantly lower than at pH 4 because the divalent anion is subject to greater repulsion. This phenomenon can be determined for all tested membranes.

All in all, the anion concentration in the retentate is enhanced compared to the permeate, especially at pH 4 and 7, primarily evoked by the retention of molybdenum. Therefore, the potential difference becomes negative and forces the permeation of corresponding ions. In the ternary experiments, Na^+ and H^+ (see Table 3.4) act as counter ions but their concentration as well as their retention was not determined. In the following quaternary experiments cobalt participates as additional counter ion.

3.3.2 Quaternary Experiments with *Ge*, *Mo*, *Re*, and *Co*

In the next step *Co* (2.0 mg L^{-1}) was added to the synthetic feed solution to evaluate the influence of a divalent cation on the retention of the anion forming elements (*Ge*, *Mo*, *Re*). The retention observed are shown in Figure 3.4.

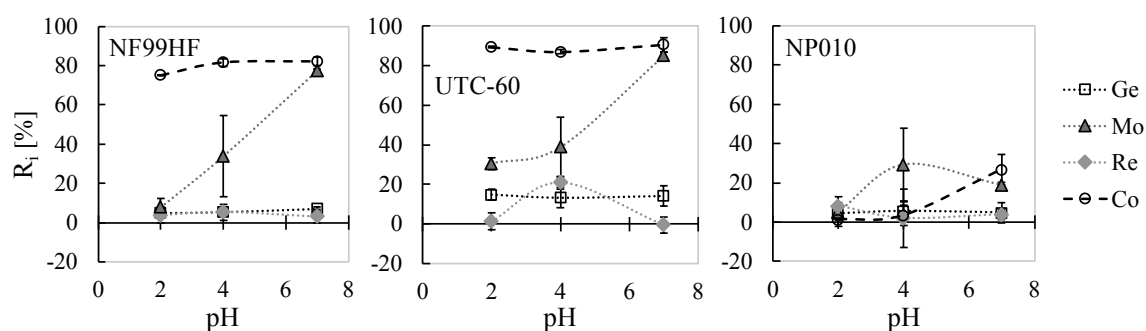


Figure 3.4. pH-dependent retention R_i of the combined elements *Ge*, *Mo*, *Re*, and *Co* in dead-end set-up (TMP: 15 bar, T: 25°C, N: 500 rpm) for the NF99HF, UTC-60, and NP010.

pH-dependent Co Retention

The NF99HF and UTC-60 show constant high cobalt retentions between 75–94% (see Figure 3.4). In the investigated pH range, the cation Co^{2+} is dominated in the aqueous solution [71,72]. Charge interactions may only have a little effect on the separation performance because a size exclusion of Co^{2+} , with a hydrated radius of 0.423 nm [64], is more appropriate. Due to the smaller MWCO of the UTC-60, the cobalt retention is slightly increased in comparison to the NF99HF. In contrary, the *Co* retention is strongly

diminished for the NP010 especially at pH 2 and 4 ($\leq 10\%$). Due to the enhanced MWCO of the NP010 (1000 Da), the divalent Co species is not rejected. At pH 7, the retention has increased up to 34%. This could be explained by the presence of the monovalent species $Co(OH)^+$, which starts to form under neutral conditions [71,72]. The $O-H$ distance in water is respectively between 96–110 pm [59,73]. Therefore, the steric hindrance is enhanced because the radius of the hydrolyzed species is enlarged compared to Co^{2+} . The precipitation of $Co(OH)_2$ seems not responsible for the increased retention because a flux decline, as consequence of scaling, was not observed and the hydroxide is mainly formed above pH 8 [71,72].

Mutual Interactions

In the quaternary experiments Co^{2+} can act as counter ion and thus, the potential difference of the anions should have changed (see Table 3.9) compared to the ternary experiments (see Table 3.8).

Table 3.9. Potential difference $\Delta\phi$ of the charged solutes between the bulk solutions for the quaternary experiments.

pH	Ionic species	$\Delta\phi$ [mV]		
		NF99HF	UTC-60	NP010
2	ReO_4^-	-1.0	-0.4	-2.2
	Co^{2+}	17.9	28.9	0.2
4	ReO_4^-	-1.4	-6.0	-1.0
	$HMoO_4^-$	-2.8	-3.3	-2.3
	MoO_4^{2-}	-2.7	-3.2	-2.2
	Co^{2+}	21.7	26.4	0.5
7	ReO_4^-	-0.8	0.1	-1.0
	MoO_4^{2-}	-19.1	-24.4	-2.7
	Co^{2+}	22.1	30.5	4.0
	$Co(OH)^+$	44.2	61.1	8.0

At pH 2, ReO_4^- acts as main counter ion for Co^{2+} . In contrary, at pH 4 and 7, the molybdate anions contribute to charge balancing. As consequence, the potential difference, especially for MoO_4^{2-} is less negative compared to the ternary experiment. Due to the enhanced MWCO of the NP010 cobalt is not rejected and thus, the MoO_4^{2-} anion is transferred into the permeate for charge balancing. As result, the Mo retention is strongly decreased (see Figure 3.4) in comparison to the ternary experiment (see Figure 3.2). Therefore, the potential differences of the NP010 are significantly different at pH 7 compared to the NF99HF and UTC-60 (see Table 3.9). Consequently, no further

experiments were conducted with the NP010 because the membrane is non-selective for the proposed separation task. The manufacturer recommends a compaction of the membrane network under 40 bar to achieve a higher selectivity. However, this was not possible in the tested dead-end set-up because the batch cell is restricted to 20 bar.

3.3.3 Influence of the main Components *Cu* and *Zn* on the Separation Selectivity

Zinc (*Zn*) is the main component in the leaching solution followed by iron (*Fe*) and copper (*Cu*, see Table 3.2). Under acidic, oxidizing leaching conditions iron is mainly present as Fe^{3+} [18–20,74] but above pH 3 iron(III) hydroxide is precipitated [74]. Therefore, the pH-dependent retention of *Fe* was not investigated. For the experiments, copper (10 mg L⁻¹) was added first to the multicomponent solution (see Figure 3.5) and subsequently zinc (10 mg L⁻¹) (see Figure 3.6).

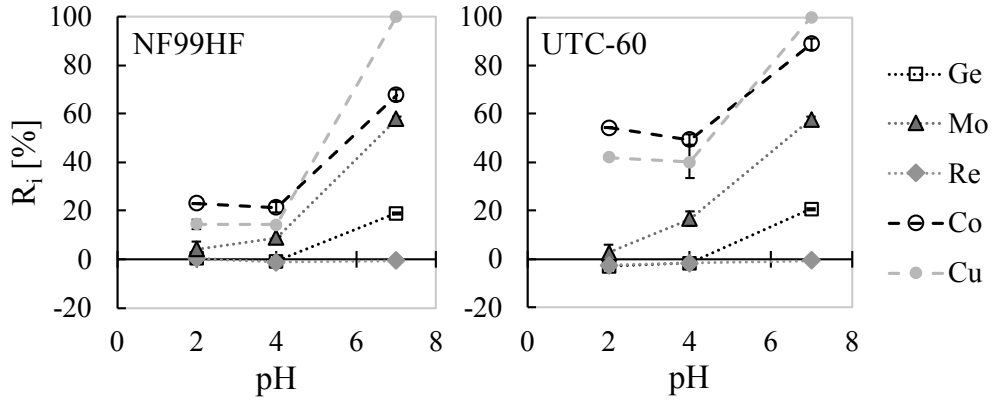


Figure 3.5. pH-dependent retention R_i of the combined elements Ge, Mo, Re, Co, and Cu in dead-end set-up (TMP: 15 bar, T : 25°C, N : 500 rpm) for the NF99HF and UTC-60.

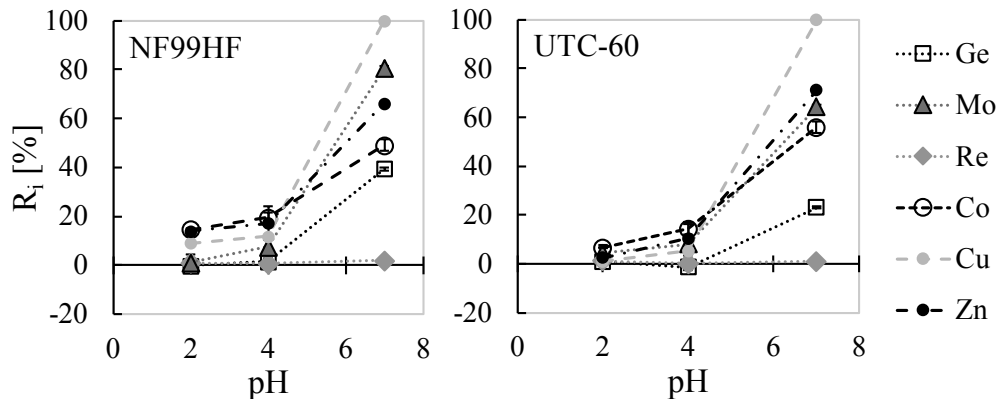


Figure 3.6. pH-dependent retention R_i of the combined elements Ge, Mo, Re, Co, Cu, and Zn in dead-end set-up (TMP: 15 bar, T : 25°C, N : 500 rpm) for the NF99HF and UTC-60.

pH-dependent Cu Retention

Considering the fact that the cobalt retention was constantly high in the investigated pH range (see Figure 3.4), the same was expected for copper. However, the pH-dependent species distribution diagram of $Cu(II)$ slightly differs from $Co(II)$ and is shown in Figure 3.7.

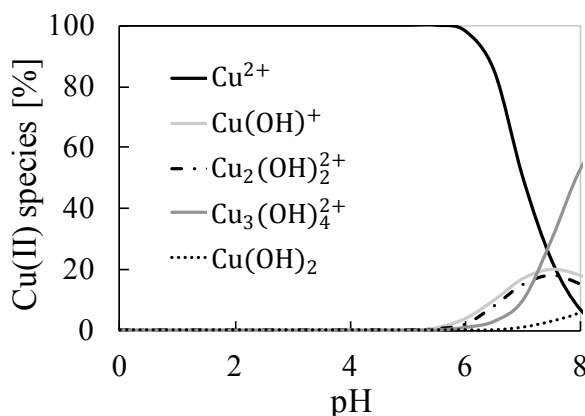


Figure 3.7. Species distribution diagram of $Cu(II)$ in aqueous solution as function of pH [75]

The dominating copper species below pH 6 is Cu^{2+} (see Figure 3.7). At pH 2 and 4, the copper retention is lower than from cobalt (see Figure 3.5), which could be explained by the smaller hydrated radius of 0.419 nm [64]. However, the cobalt retention is significantly decreased compared to the quaternary experiments. The enhanced ionic strength of the feed solution and thus, the build-up concentration as well as the electric field gradient forces the permeation of the solutes. Moreover, the increased presence of sulfate (SO_4^{2-}) needs to be considered. The sulfate retention was between 20–30% at pH 2 and thus, the permeation of the divalent cations supported for charge balancing. Furthermore, it can be assumed that the cations have lost hydration water and due to this, the permeation is enhanced and consequently the retention decreased. Nevertheless, due to the smaller MWCO of the UTC-60, the Co and Cu retention is higher compared to the NF99HF.

At pH 7, the Cu retention is increased up to 99.9% and Co achieves nearly the same values as in the experiment without copper. Above pH 6, the Cu species changes and the hydrolyzed hydroxide species (see Figure 3.7) becomes relevant for the separation performance. Due to steric hindrance, the retention is increased. The precipitation of $Cu(OH)_2$, which is bluish in color, was not observed.

pH-dependent Zn Retention

In the investigated pH range zinc is present as Zn^{2+} with a hydrated radius of 0.430 nm [64]. Therefore, a high retention evoked by size exclusion was expected but as shown in Figure 3.6 relatively low retentions were achieved at pH 2 and 4 ($\leq 17\%$). Under acidic conditions all elements remain as ions in the aqueous solution and the build-up concentration and electric field gradient is strongly enhanced. Therefore, less cations are rejected because the bulk solutions strive toward electroneutrality. Furthermore, the hydrated radius seems additionally reduced and consequently, the retention decreased because the permeation is enhanced.

At pH 7, the retention is increased because $Zn(OH)^+$ is formed [76] similarly to copper and cobalt. The precipitation of $Zn(OH)_2$ mainly starts at pH 8 [76] and seems not responsible for the increased retention because scaling was not observed and the retentate was still free from precipitates, which may be whitely colored.

Mutual Interactions

The separation selectivity is increased at pH 7 (see Figure 3.5/Figure 3.6) due to the presence of the formed monomeric metal hydroxides and a separation of rhenium seem feasible. To evaluate occurring mutual interactions, the selectivity $S_{i,j}$ was calculated after Eq. 10 and the results are shown in Figure 3.8.

$$S_{i,j} = \frac{c_{i,P}/c_{j,P}}{c_{i,R}/c_{j,R}} \quad (10)$$

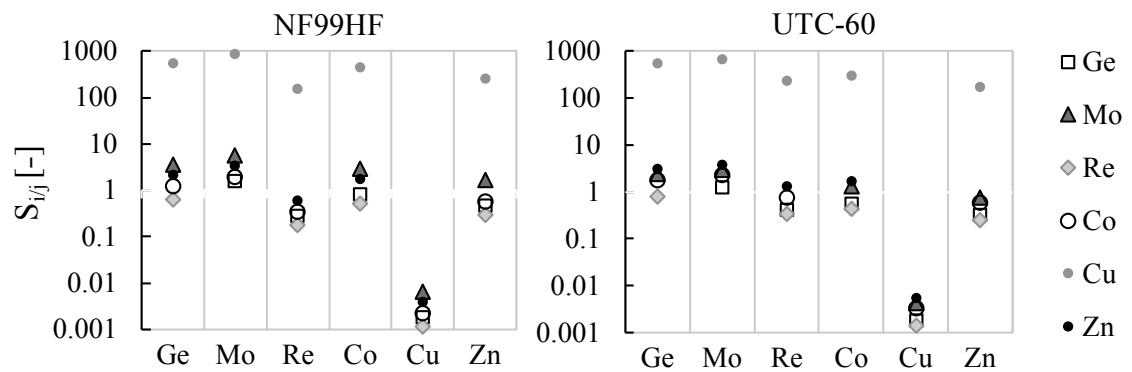


Figure 3.8. Selectivity $S_{i,j}$ of the combined elements Ge, Mo, Re, Co, Cu, and Zn at pH 7 in dead-end set-up (TMP: 15 bar, T : 25°C, N : 500 rpm) for the NF99HF and UTC-60.

All elements show an extremely high selectivity towards copper (see Figure 3.8). Conducted precipitation experiments at pH 10 conclude that *Mo* and *Ge* are co-

precipitating with *Cu*. This indicates a high affinity of these elements towards copper and could explain the increased *Ge* retention at pH 7 (see Figure 3.5) in comparison to the ternary experiments (see Figure 3.2). During the experiments precipitation was not observed and it can be assumed that the presence of *Cu* and additional *Zn* (see Figure 3.6) supports the formation of $GeO(OH)_3^-$, which begins to form at pH 7 [49,50] and related repulsion leads to an enhanced *Ge* retention.

However, the experimental results indicate that a separation during concentration cannot be realized under acidic conditions in dead-end set-up because a high shear force and the build-up concentration as well as the electric field gradient forces the permeation of the solutes. Nevertheless, a selective separation at pH 2 seems to be most practicable because bioleaching is conducted under acidic conditions and a pH adjustment would be associated with higher costs in the technical implementation. Therefore, the recovery was reduced to 10% (see Figure 3.9) to investigate if the separation selectivity can be increased due to the fact that size and dielectric exclusion should be more dominant because the permeation is less forced.

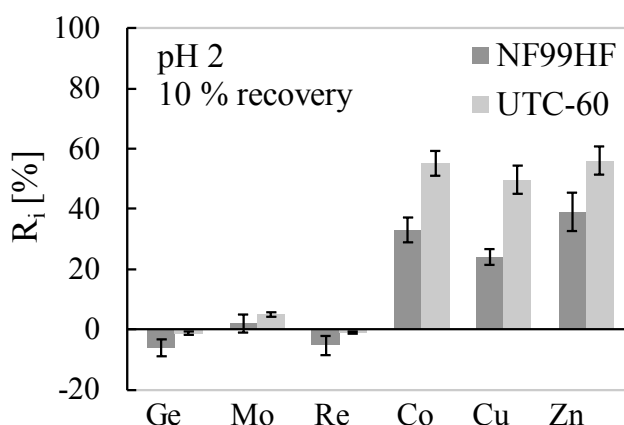


Figure 3.9. Retention R_i of the combined elements *Ge*, *Mo*, *Re*, *Co*, *Cu*, and *Zn* for a recovery of 10% at pH 2 in dead-end set-up (TMP: 15 bar, T : 25°C, N : 500 rpm) for the NF99HF and UTC-60.

As shown in Figure 3.9, the separation selectivity is enhanced in the case that the recovery is reduced from 50% (see Figure 3.6, pH 2) to 10%. The retention of $Ge(OH)_4^0$ is lower in comparison to $H_2MoO_4^0$ due to the fact that the steric hindrance is decreased. The ReO_4^- retention is still negative and suggests that the permeation is forced because the perrhenate is attracted from the positively charged membrane surface at pH 2 and steric hindrance is negligible. The retention of the cations decreases in the order Zn^{2+} (0.430 nm) > Co^{2+} (0.423 nm) > Cu^{2+} (0.419 nm) and confirms that the retention is mainly based on size exclusion. Furthermore, the UTC-60 shows overall higher retentions compared to the

NF99HF due to the smaller MWCO. However, a lower recovery cannot be tested in dead-end set-up because the dead volume from the sinter disc (approx. 20 mL) needs to be flushed out (see Figure 3.1).

Nevertheless, the results at pH 2 indicate that a separation between the anion forming elements (*Ge*, *Mo*, *Re*) and cations (*Co*, *Cu*, *Zn*) is possible. It can be assumed, that the selectivity can be increased even more by lower filtration pressures and enhanced stirring rates because shearing forces in flow direction should be reduced and the horizontal shear stress enhanced. Nonetheless, further investigations shall be conducted in cross-flow set up with varying e.g. transmembrane pressures and flow velocities. The changed process conditions should influence the separation performance positively.

3.4 Conclusion

The present paper aimed at investigating the pH-dependent separation performance of the strategic elements *Co*, *Cu*, *Ge*, *Mo*, *Re*, and *Zn* to determine dominating retention mechanisms, mutual interactions, and the separation selectivity during concentrating. Three polymeric nanofiltration membranes (NF99HF, UTC-60, NP010) were utilized and experiments were performed in dead-end set-up (*TMP*: 15 bar, *T*: 25°C, *N*: 500 rpm). The composition of the feed solution was related to the bioleached Theisen sludge, a waste by-product from German copper ore smelting including various strategic elements. In ternary experiments (*Ge*, *Mo*, and *Re*), the retention of germanium and rhenium was relatively low in the investigated pH-range ($\leq 22\%$). A charge exclusion can be excluded for germanium, which is present as uncharged germanic acid ($Ge(OH)_4^0$) and a size exclusion is negligible. For the perrhenate (ReO_4^-), charge exclusion was only determined for the NF99HF and NP010 above the isoelectric point, where repulsion leads to an enhanced retention. Otherwise, the perrhenate was not rejected since a steric hindrance was not determined. Moreover, attraction mechanisms between ReO_4^- and positively charged membrane surface below the IEP supported the permeation. The *Mo* retention was strongly pH-dependent and enhanced with increasing pH because the *Mo* species is changing and repulsion as well as steric hindrance is more pronounced.

For the quaternary experiments, cobalt was added to the feed solution. The *Co* retention of the tested membranes varied and achieved values $\geq 75\%$ for the NF99HF and UTC-60, which was mainly based on size exclusion. In contrast, cobalt was almost not rejected at all by the NP010 due to the enhanced MWCO. As a consequence, the *Mo* retention was significantly decreased compared to the ternary experiment due to charge balancing.

In the presence of the main components *Cu* and *Zn*, the separation performance was diminished under acidic conditions. During concentrating, the concentration and electric field gradient is steadily increasing and thus, the permeation of the uncharged solutes, anions, and cations is forced because the membrane strives to establish equilibrium conditions. Furthermore, the flow direction in dead-end forces the permeation of the solutes and the ions can lose hydration water and thus, the ionic permeability is enhanced. Nevertheless, the separation selectivity can be increased by keeping the recovery and ionic strength of the solution low. Moreover, a separation of rhenium from the multicomponent solution seems feasible at pH 7 because all elements besides rhenium change the ionic species and are mainly rejected by size.

Overall, nanofiltration is a promising technique for the separation of strategic elements from multicomponent leaching solutions and could be used for pre-fractionation, which should reduce the consumption of energy and chemicals in subsequent processes. The application of the tested membranes NF99HF and UTC-60 seems also conceivable for related separation tasks. It can be assumed that changed hydrodynamic conditions in cross-flow affect the separation performance positively. The tangential surface flow should lead to higher retentions, especially of the cations and thus, to a higher selectivity towards the anion forming elements. Hence, further investigations aimed to increase the selectivity in cross-flow set-up under acidic conditions by varying the process parameters (e.g. flow velocity, transmembrane pressure, temperature).

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4. Influence of Membrane Characteristics

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Characterization and performance evaluation of polymeric nanofiltration membranes for the separation of strategic elements from aqueous solutions

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Abstract

Nanofiltration (NF) can be used for the separation of mono- and divalent ions as well as for uncharged solutes, such as strategic elements from aqueous solutions. In dependence of pH and feed solution concentration, the element species and membrane charge may vary, which can strongly affect the separation performance. The aqueous solution of interest is acidic, sulfate-rich, and originated from a microbial leaching process of an accrued flue dust from German copper ore smelting with various strategic elements included. The separation of *Ge*, *Mo*, *Re*, *Co*, *Cu*, and *Zn* was evaluated in a cross-flow set-up (flow velocity: 0.5 m s⁻¹, transmembrane pressure: 10–20 bar). For fundamental understanding, the flux, permeability, and separation performance of the utilized polyamide NF membranes (NF99HF, UTC-60) were investigated with *NaCl* and *MgSO₄* and compared to those of the strategic elements. Moreover, the surface characteristics of the membranes were analyzed by AFM, SEM, FTIR, contact angle analysis, and streaming potential measurements. The utilized membranes show differences regarding e.g. morphology, smoothness, and location of the isoelectric point. Nevertheless, the experimental results indicated that *Re* and *Ge* can be separated from the multicomponent solution with both tested membranes.

4.1 Introduction

NF membranes can be used for a wide field of applications, including e.g. wastewater treatment, drinking water production, and water softening. NF is a pressure driven process with properties between reverse osmosis (RO) and ultrafiltration (UF) [1–3]. Suspensions or emulsions as well as solutions including molecular compounds can be separated by UF membranes, which have a porous structure [2,4]. RO membranes with a dense structure demineralize and have no selectivity towards monovalent ions [2,4,5]. However, with NF membranes it is possible to separate mono- ($R_i < 50\%$) and divalent ($R_i > 90\%$) ions from aqueous solutions but with moderate pressures than in RO [2].

In the recent years, the application of polymeric membranes for metal ion separation has been established [6–8] and heavy metal ions like *As*, *Co*, and *Pb* can be removed from aqueous solutions [8–11]. The retention is strongly influenced by the effective ionic radius and the molecular weight plays a subordinated role [6]. Moreover, the retention is affected by pH and feed concentration [7,8,12]. The treated solution can have various compositions and thus, the utilized membranes need to have adequate properties because, in addition to the feed, the membrane characteristics as well as the operating conditions affect the separation performance [3,7,8,12,13].

Several studies show that membrane surface properties such as morphology and structure govern the membrane performance [14–16]. Composite NF membranes, which are frequently utilized and often manufactured by interfacial polymerization [3,6], have a dense selective thin film active layer ($\leq 1 \mu\text{m}$) and a porous support layer (50–150 μm) [2]. The surface chemistry and morphology of the top layer is mainly responsible for the separation performance of the membrane [17]. The effective pore radius r_p , effective membrane thickness over porosity $\Delta x/A_k$, and membrane charge density X_d are typically membrane characteristics to predict the rejection of uncharged solutes and salts [59]. By atomic force microscopy (AFM), the surface pore radius and surface porosity can be determined [1,18,19]. Moreover, the pore radius can be estimated using uncharged solutes and applying a mathematical model to experimental data [1]. Most commonly, the steric hindrance pore (SHP) model is used and thus, the pore radius can be calculated according to Eq. 1 if the solute radius r_s is known and the reflection coefficient σ is determined [20,21].

$$\sigma = 1 - \left(1 + \frac{16r_s^2}{9r_p^2}\right) \left(1 - \frac{r_s}{r_p}\right)^2 \left[2 - \left(1 - \frac{r_s}{r_p}\right)^2\right] \quad (1)$$

If the pore radius is known, the Hagen-Poiseuille equation (see Eq. 2), which describes the relation between the pure water flux J_w (η – dynamic viscosity of the solution) and the applied pressure across the membrane ΔP , can be used to estimate $\Delta x/A_k$ [1,21,22].

$$J_w = \frac{r_p^2 \Delta P}{8\eta (\Delta x/A_k)} \quad (2)$$

The SHP model cannot be applied for charged solutes as electrostatic interactions occur due to the fact that the membrane may be charged. By streaming potential measurements, the zeta potential and thus, the surface charge of the membrane can be estimated [23–25]. To predict the permeate flux J_i and retention of a single salt solution, the DSPM-DE (Donnan steric pore model – dielectric exclusion) model, which is based on the extended Nernst-Planck equation (see Eq. 3), can be applied [1,26]. The transport of an ion i is contributed by a diffusive, electrical, and convective term as shown in Eq. 4.

$$J_i = -D_{i,p} \frac{dc_i}{dx} - \frac{z_i F c_i D_{i,p}}{RT} \frac{d\phi}{dx} + K_{i,c} c_i V \quad (3)$$

$$J_i = J_{i,diffusive} + J_{i,electrical} + J_{i,convective} \quad (4)$$

$D_{i,p}$ – hindered diffusivity, $\frac{dc_i}{dx}$ – concentration gradient across the active layer, z_i – charge number, c_i – solute concentration, $\frac{d\phi}{dx}$ – potential gradient over the active layer of the membrane, T – temperature, F – Faraday constant, R – ideal gas constant, $K_{i,c}$ – convective hindrance factor, c_i – solute concentration, V – velocity of permeation

In the present paper, the separation performance for different strategic elements (Co , Cu , Ge , Mo , Re , and Zn) shall be explained by size, Donnan, and dielectric exclusion. The feed composition is originated from a bioleaching process of a blast-furnace flue dust accrued from German copper ore smelting [27,28]. The target elements are present as neutral solutes, anions, and cations and shall be separated by polymeric NF membranes. The membrane characterization is required to describe the membrane separation performance more detailed. Therefore, the topography (roughness) and cross-section morphology of two thin-film composite membranes (NF99HF, UTC-60) were analyzed by SEM and AFM. The hydrophobicity of the membranes was detected by contact angle measurements and the surface chemical functionality was obtained by ATR-FTIR. With the help of streaming potential measurements, the zeta potential was determined. Moreover, the separation performance of $NaCl$ and $MgSO_4$ was investigated and compared to those of the strategic elements.

4.2 Materials and Methods

4.2.1 Nanofiltration Membranes

Two commercial polymeric NF membranes (NF99HF, UTC-60) were utilized to evaluate the separation performance of the target strategic elements from a sulfate-rich, acidic aqueous solution. The membranes were chosen due to their good separation selectivity in previous investigations [29–34]. The support material of both membranes is similar but the material of the active layer slightly differs as shown in Table 4.1. Moreover, the molecular weight cut-off and the location of the isoelectric point differ from each other, which can refer to varying retentions

Table 4.1. Characteristics of the utilized NF membranes taken from the literature. Unmarked information was provided by the manufacturer.

Characteristic	Membrane	
	NF99HF	UTC-60
Manufacturer	Alfa Laval AB (Sweden)	Toray Ind. Inc. (Japan)
Nomenclature	Thin-film composite	Thin-film composite
Active layer	Polyamide	Poly(piperazine)amide
Support layer	Polysulfone	Polysulfone
Support paper	Polyester	Polyester
MWCO [Da]	200	150–300
T_{max} [°C]	50	45
p_{max} [bar]	55	41
pH range	3–10	3–8
IEP [pH]	4.1–4.4 ^{a)} (0.01 M NaCl)	3.2 ^{c)} (20 mM NaCl + 1 M NaHCO ₃)
R_i [%]	NaCl	72 ^{b)}
	Na ₂ SO ₄	97 ^{b)}
	MgSO ₄	≥98
L_p^* [kg m ⁻² h ⁻¹ bar ⁻¹]	9–18 ^{b)}	10 ^{e)} –15 ^{f)}

*pure water

^{a)}[35], ^{b)}[36], ^{c)}[37], ^{d)}[38], ^{e)}[39], ^{f)}[40]

4.2.2 SEM Analysis

The cross-section morphology of the membranes was analyzed by a scanning electron microscope (SEM) using a Quanta Feg 250 by FEI. Images were taken in a high vacuum (10⁻⁵–10⁻⁶ mbar) in SE (secondary electrons) mode. The acceleration voltage was set to

2 kV. The residence time for each scanned area was 100 ns. The magnification of the SEM images was 250, 1000, and 10000. The aim was to investigate the thickness of the active layer, which is proportional to permeation rate of the membrane [14].

4.2.3 AFM Analysis

The membrane topography was analyzed by using a XE-100 atomic force microscope (AFM, Park Systems Corp.) to investigate the surface roughness, which is related to colloidal fouling [14]. The imaging was performed at room temperature in tapping mode in air. A cantilever Tap190 Al-G from Budget Sensors® with a spring constant of 21.9 N m^{-1} , a tip radius $<10 \text{ nm}$, and a resonant frequency of 128 kHz was used. High-resolution topographic images were made with a scanning speed of 0.3 Hz. The amplitude ratio (A/A_{sp}) for all images was between 0.73 and 0.75. To remove scanning induced curvatures and slopes, the images were flattened with a second order polynomial approximation to calculate the average roughness R_a and the root mean squared roughness R_q according to Eq. 5 and 6 [16].

$$R_a = \frac{1}{S} \cdot \int_0^S |z(x)| dx \quad (5)$$

$$R_q = \sqrt{\frac{1}{S} \cdot \int_0^S z^2(x) dx} \quad (6)$$

S– mean plane of the surface, *z*– vertical dimension, *x*– horizontal dimension

No preparative procedures were used, which may affect the membrane structure. The membrane roughness was determined by scanning a surface area of $5 \times 5 \text{ }\mu\text{m}$ and $2 \times 2 \text{ }\mu\text{m}$. To determine the pore size and pore size distribution on the active layer surface, a higher magnification of $40 \times 40 \text{ nm}$ would have been required [41], which was hampered by the utilized cantilever.

4.2.4 Contact Angle Analysis

The contact angle between water and membrane surface was measured with an OCA 50 (DataPhysics Instruments GmbH) in sessile drop mode to determine the hydrophobicity of the utilized membranes, which is correlated to the flux [42,43]. The video system used had a measuring range between 0 and 180° with a measuring precision of 0.1° .

4.2.5 FTIR Analysis

The active layer of the membranes was analyzed by attenuated total reflection-fourier transform infrared (ATR-FTIR) spectroscopy using a Thermo Scientific Nicolet 380 FTIR spectrometer to provide elemental and chemical information [44]. The aim was to verify the presence of characteristic functional groups, which are mainly responsible for the amphoteric surface charge of the membrane [17]. For the analysis, a smart orbital diamond crystal plate (3 mm diameter, 45° incident angle) by Thermo Fisher Scientific was used as an internal reflection element. All spectra were scanned 32 times at 6 cm⁻¹ resolution and radioed to background spectra, which were recorded in air. The penetration depth between the wave numbers of 4000 and 400 cm⁻¹ was approximately 5 µm.

4.2.6 Zeta Potential Measurements

The functional groups, which are located on the active surface layer, influence the surface charge density of the membrane. Related interactions between charged membrane surface and charged solute can affect the membrane performance. The zeta potential and thus, the surface charge of the membrane can be determined by streaming potential measurements. By the Helmholtz-Smoluchowski equation, using the Fairbrother and Mastin approach, the relationship between the measurable streaming potential ΔE and the zeta potential ζ can be expressed according to Eq. 7 [17,23–25,45].

$$\zeta = \frac{\Delta E \eta k_s}{\Delta P \epsilon_0 \epsilon_R} \quad (7)$$

ΔP – applied pressure, η – dynamic viscosity of the solution, k_s – specific conductivity of the solution, ϵ_0 – dielectric permittivity in vacuum, ϵ_R – dielectric constant of the medium

The streaming potential measurements were conducted with a SurPASS Electrokinetic Analyzer (AntonPaar GmbH). The target pressure was 300 mbar and the flow rate 100 mL min⁻¹. The zeta potential was determined with 1 mM NaCl, 1 mM MgSO₄, and the synthetic feed solution in a pH range between 2 and 5. pH adjustment was conducted with 0.1 M HCl for NaCl and with 0.1 M H₂SO₄ for MgSO₄ and the synthetic feed solution.

4.2.7 Synthetic Feed Solution

The utilized feed solution (see Table 4.2) is a model solution of a leached secondary mining resource, the so called Theisen sludge [27]. The sludge remains from German

copper ore smelting and contains various strategic elements in a wide concentration range [28]. By bioleaching, the bonded metals can be solubilized from the mineral phase and remain as ions in the solution [46], which is acidic (pH 2–3) and sulfate-rich (approx. 3000 mg L⁻¹) [27]. The target elements (e.g. *Ge*, *Re*) shall be separated from the multicomponent solution by different element specific procedures like NF [30].

Table 4.2. Composition of the synthetic feed solution and the present ionic species.

Element	$c_{i,F}$ [mg L ⁻¹]	Chemical compound	Purity [%]	Manu- facturer	Ionic species [pH 2]	r_h [nm]
<i>Mo</i>	0.5	Sodium molybdate(VI) dihydrate	98.0	Alfa Aesar	$H_2MoO_4^{0a)}$	0.247 ^{g)}
<i>Ge</i>	1.0	Germanium(IV) dioxide	99.999	Alfa Aesar	$Ge(OH)_4^{0b)}$	0.206 ^{g)}
<i>Re</i>	1.0	Sodium perrhenate(VII)	99+	Alfa Aesar	$ReO_4^{-c)}$	0.352 ^{h)}
<i>Co</i>	2.0	Cobalt(II) sulfate heptahydrate	99+	AnalaR Normapur	$Co^{2+d)}$	0.423 ^{h)}
<i>Cu</i>	100	Copper(II) sulfate	≥99.0	Sigma Aldrich	$Cu^{2+e)}$	0.419 ^{h)}
<i>Zn</i>	3000	Zinc(II) sulfate monohydrate	≥99.0	Sigma Aldrich	$Zn^{2+f)}$	0.430 ^{h)}

a)[47], b)[48,49], c)[50], d)[51], e)[52], f)[53], g)[54], h)[55]

As shown in Table 4.2, the feed solution is quite complex and contains uncharged and charged solutes. The wide range of concentrations renders the separation task more challenging. The pH of the feed solution was adjusted with 1 M H_2SO_4 to pH 2. The concentration of *Ge*, *Re*, *Mo*, and *Co* was measured with ICP-MS (Agilent Technologies Inc., 7700 Series). As consequence of the expected higher *Cu* and *Zn* concentration, an ICP-AES (Spectro Analytical Instruments GmbH, Ciros) was used for these measurements.

4.2.8 Experimental Cross-flow Set-up

The flux and the retention of the membranes were determined in cross-flow set-up (see Figure 4.1) using deionized water, 1 mM $NaCl$, and 1 mM H_2SO_4 . By ion chromatography (Metrohm AG, 850 Professional), the anions Cl^- and SO_4^{2-} as well as the cations Na^+ and Mg^{2+} were detected to verify the concentration of the $NaCl$ and

$MgSO_4$ solution. Furthermore, the separation performance of the membranes was evaluated using the synthetic feed solution.

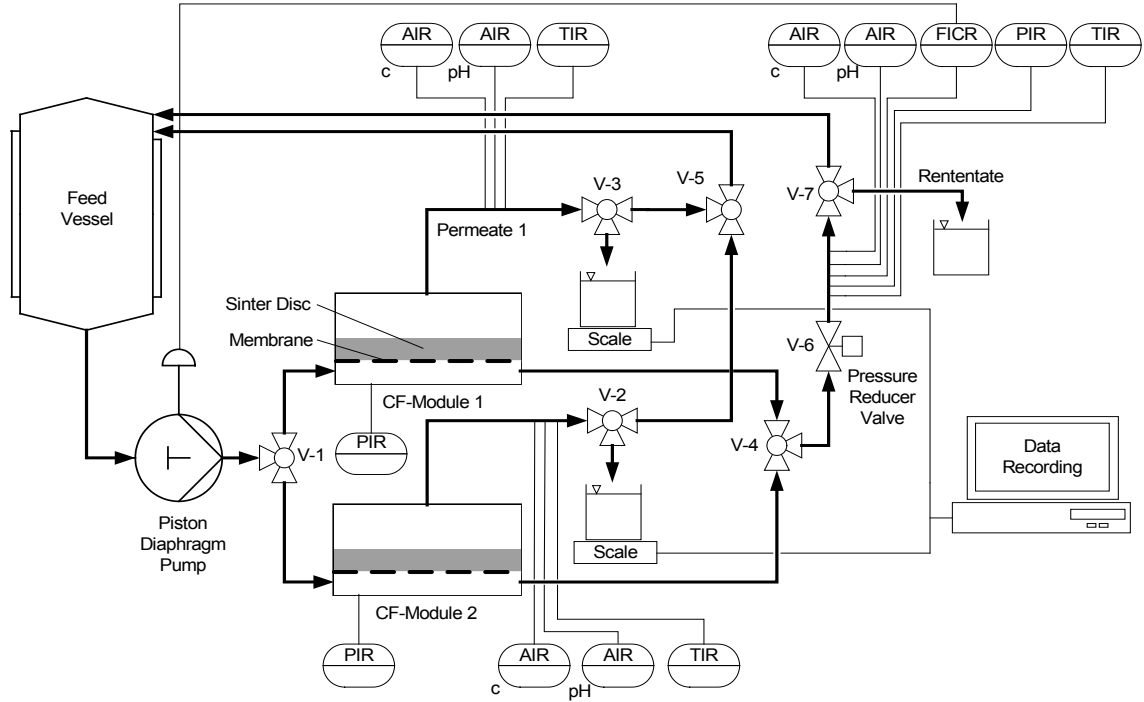


Figure 4.1. Flowchart of the cross-flow set-up.

The utilized membrane with an active surface area of 76 cm² (each module) was installed upon a sinter disc, which provided mechanical resistance. Two modules were connected parallelly to perform a double determination. The feed was delivered by a piston diaphragm pump (Verder Deutschland GmbH & Co. KG, Typ G03) and the required transmembrane pressure (10, 15, and 20 bar) was built up by a pressure reducer valve (Badger Meter Europa GmbH, Typ RC 200). The cross-flow velocity (0.5 m s⁻¹) was adjusted by the pump's flow rate and controlled by a flow meter (Meister Strömungstechnik GmbH, Typ DHGA-10). During the experiments, the transmembrane pressure and temperature (25°C) were kept constant. The permeate was filtered through the membrane and was led out pressureless. Received permeate was weighted on a precision scale (Kern & Sohn GmbH, Typ PCB 2500, readout: 0.01 g).

The flux J_i (see Eq. 8) was calculated by the ratio of the permeate mass flow $\dot{m}_p$ to the membrane surface area A .

$$J_i = [kg\ m^{-2}\ h^{-1}] = \frac{\dot{m}_p}{A} \quad (8)$$

Moreover, the permeability L_p of the membranes was determined according to Eq. 9.

$$L_p = [kg\ m^{-2}\ h^{-1}\ bar^{-1}] = \frac{\dot{m}_p}{A \cdot \Delta P} \quad (9)$$

To evaluate the separation performance of the utilized polymeric NF membranes, the retention R_i (see Eq. 10) of each ion i was calculated by comparing the concentration of the permeate $c_{i,P}$ to those in the feed $c_{i,F}$.

$$R_i = [\%] = \left(1 - \frac{c_{i,P}}{c_{i,F}}\right) \cdot 100\% \quad (10)$$

4.3 Results and Discussion

4.3.1 SEM Analysis

The cross-section morphology of the NF99HF and UTC-60, which was analyzed by SEM, is shown in Figure 4.2 for different magnifications.

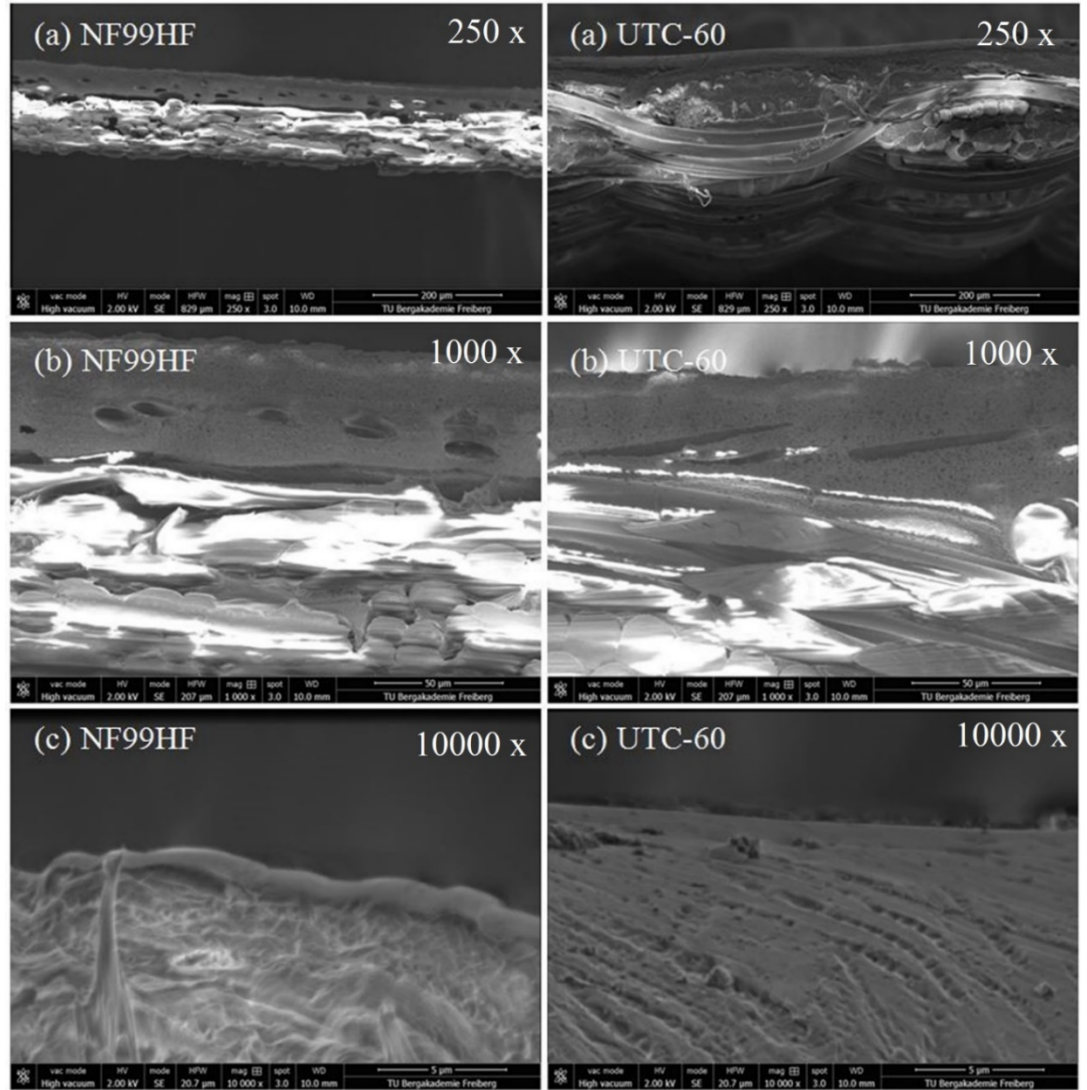


Figure 4.2. SEM images of the cross-section morphology of the NF99HF and UTC-60 for a magnification of (a) 250 x, (b) 1000 x, and (c) 10000 x.

The cross-section (see Figure 4.2(a)) of the NF99HF shows the typical morphology of a thin-film composite membrane and the support layer can be clearly distinguished from the support paper. In comparison, the UTC-60 has a woven support paper structure. Due to this, the support layer is not homogenously distributed. Moreover, the support layer (see Figure 4.2(b)) of the UTC-60 shows elongated macro-void formations while those of the NF99HF resemble spheres. The thickness of the active layer was determined with a magnitude of 10000 (see Figure 4.2(c)) and is almost equal for both membranes (NF99HF: $0.93 \pm 0.17 \mu\text{m}$; UTC-60: $0.94 \pm 0.06 \mu\text{m}$). In the literature an active surface layer thickness $\leq 1 \mu\text{m}$ is reported for NF membranes [2], which corresponds with the conducted SEM analysis. Nevertheless, the permeation rate of the membrane is proportional to the thickness of the active layer [14]. Therefore, the separation performance for the utilized membranes should not deviate significantly from each other.

4.3.2 AFM Analysis

The membrane roughness R_q and R_a was measured in tapping mode for two different scanned surface areas (see Table 4.3). The AFM images for a scanned area of $2 \times 2 \mu\text{m}$ are shown in Figure 4.3 for the NF99HF and UTC-60.

Table 4.3. Root mean squared (RMS) roughness R_q and average roughness R_a (with standard derivation) of the NF99HF and UTC-60 for different scanned surface areas.

Scanned surface area [μm]	NF99HF		UTC-60	
	Membrane roughness [nm]			
	R_q	R_a	R_q	R_a
5 x 5	9.2 ± 0.3	7.3 ± 0.3	11.2 ± 0.2	8.7 ± 0.2
2 x 2	3.3 ± 0.2	2.5 ± 0.1	4.1 ± 0.1	3.1 ± 0.1

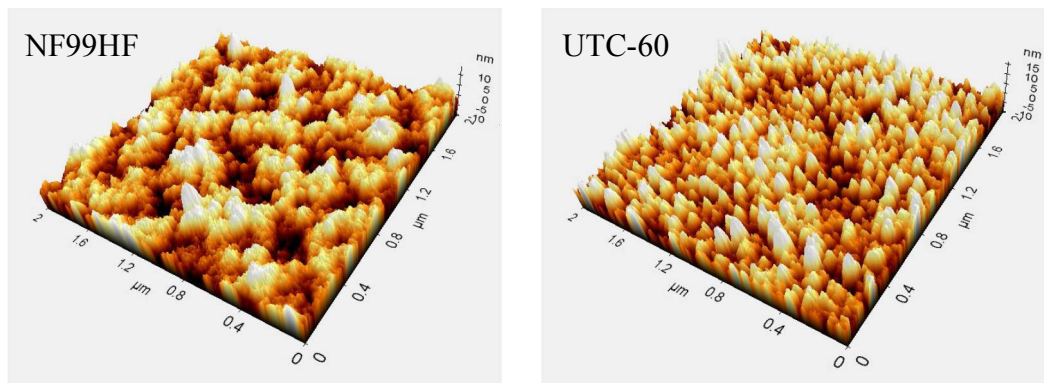


Figure 4.3. AFM tapping mode images of NF99HF and UTC-60 for a scanned surface area of $2 \times 2 \mu\text{m}$.

As shown in Table 4.3, the membrane roughness increases with increasing scanned surface area. Boussu et al. (2005) investigated the same correlation and indicated that the roughness of larger surface areas is caused by lower frequencies compared to small surface areas, which are scanned with higher frequencies [42]. As consequence, only the same scanned surface sizes of different membranes can be compared to each other. Kim et al. (2007) reported a roughness of 13.9 nm for the UTC-60 [56] and Llenas et al. (2011) a R_q of 12.3 nm for the NF99HF [57], which can be compared to the R_q data from a scanned surface area of $5 \times 5 \mu\text{m}$. The roughness results indicate that the NF99HF is smoother compared to the UTC-60, which contains more picks on the surface (see Figure 4.3). However, a rough surface might be responsible for an increased fouling and flux decline [14,42]. Further experiments shall be conducted with the bioleaching solution to investigate if fouling affects the separation process. As consequence of the rougher surface of the UTC-60, fouling should be more pronounced compared to the NF99HF.

4.3.3 Hydrophobicity Measurements

The measured contact angles with deionized water are shown in Table 4.4. Moreover, the pH was adjusted with 1 M H_2SO_4 to pH 2 because the investigated aqueous solution is acidic and sulfate-rich.

Table 4.4. Contact angles (with standard derivation) of the NF99HF and UTC-60 for deionized water (DW) and pH 2.

Media	Contact angle [°]	
	NF99HF	UTC-60
DW	34.5 ± 4.2	49.5 ± 4.9
pH 2	37.2 ± 4.0	54.9 ± 1.7

The active layer of the NF99HF is hydrophilic and has a lower contact angle compared to the UTC-60. Thus, the UTC-60 is less hydrophilic because a more hydrophobic material corresponds to a larger contact angle [42]. Madsen et al. (2014) even measured a lower contact angle ($<20^\circ$) for the NF99HF [58]. For the UTC-60 similar contact angles are reported in the literature ($51.6 \pm 5.4^\circ$) [56]. However, the surface roughness is connected with the hydrophobicity of the membrane and thus, a rough surface is less hydrophilic than a smooth one. The measured membrane roughness R_q and R_a of the UTC-60 is enhanced (see Table 4.3) and therefore, this membrane is more hydrophobic, which corresponds with the contact angle measurements. However, a higher

hydrophobicity implies a lower water flux of the membrane [43]. Thus, the more hydrophilic NF99HF should have a higher flux.

Nevertheless, the hydrophobicity of the membranes is slightly increased (respectively the contact angle is increased) in case the pH of the solution is adjusted to pH 2 (see Table 4.4). Brant et al. (2006) and Hurwitz et al. (2010) investigated the contact angle in dependence of pH and the measurements indicate that the contact angle is decreasing in case pH is increasing [59,60]. Under acidic conditions ($\text{pH} < 4$), the carboxyl groups (COOH), which are located on the polyamide membranes surface, are fully protonated. On the contrary, above pH 7, these groups are fully ionized (COO^-) [60,61]. Therefore, the membrane is less hydrophilic at pH 2 because COO^- groups are missing, which have strength of adhesion to OH groups and therefore, hydrogen bonds cannot be formed [60].

4.3.4 ATR-FTIR Analysis

The active layer of the NF99HF and UTC-60 was characterized with ATR-FTIR. The most important bands are identified in Figure 4.4 according to Table 4.5.

Table 4.5. Some characteristic ATR-FTIR bands [44,62].

Wave number [cm^{-1}]	Peak assignment
3400	<i>N-H</i> stretching (semi-aromatic membrane)
3330	<i>N-H</i> and <i>O-H</i> stretching
3300	<i>O-H</i> stretching (fully aromatic membrane)
3000–2900	Methyl group (aliphatic <i>C-H</i> stretching)
1626	Amide band I (<i>C=O</i> stretching)
1586/1488 doublet	Aromatic ring (<i>C=C</i> stretching vibration)
1503	<i>Ar-C-Ar</i> structure (<i>C-C</i> stretching band)
1385/1365 doublet	Methyl group (<i>C-H</i> bending)
1323/1295 doublet	SO_2 group (asymmetric SO_2 stretching)
1243	<i>Ar-O-Ar/aryl-O-aryl</i> (aromatic ether band)
1151	SO_2 group (symmetric SO_2 stretching band)
1045	SO_3^- group (symmetric SO_3^- stretching band)

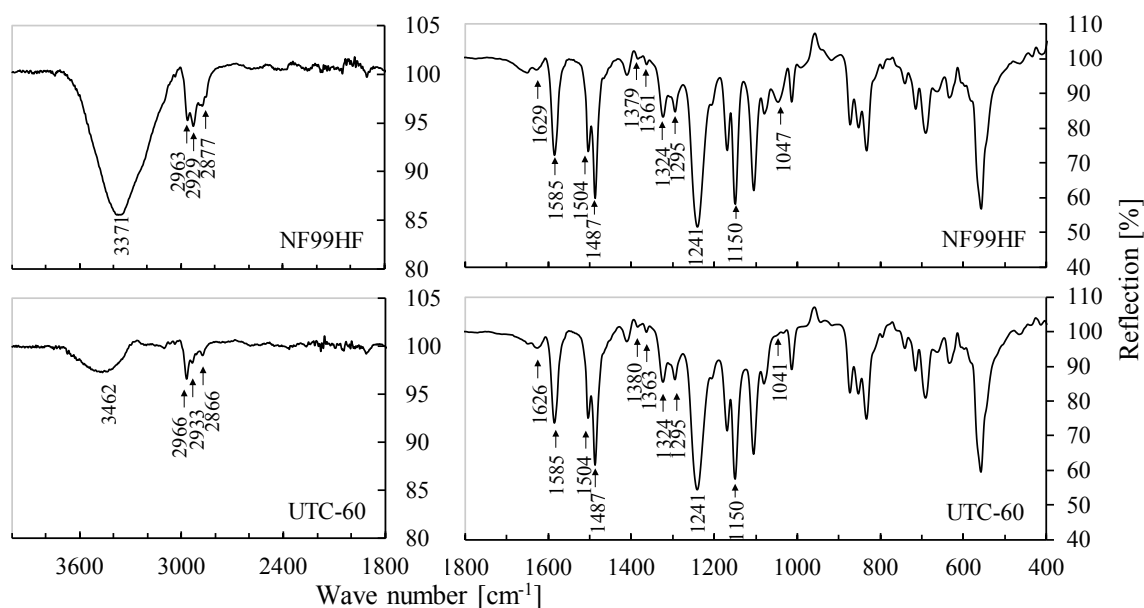


Figure 4.4. ATR-FTIR spectra of the active layer of the NF99HF and UTC-60 (most important bands were indicated).

The active layer of the NF99HF is made from polyamide and of the UTC-60 from poly(piperazine)amide. The typical $-CO-NR_2$ band ($\sim 1626\text{ cm}^{-1}$, amide band I, $C=O$ stretching) can be found for both membranes in the ATR-FTIR spectra. The main difference between both membranes is that the NF99HF is fully aromatic (see Figure 4.5) and the UTC-60 semi-aromatic (see Figure 4.6) which can be confirmed by the characteristic bands between 3300 and 3400 cm^{-1} (see Figure 4.4). Moreover, aromatic bands at 1586 and 1488 cm^{-1} ($C=C$ stretching vibration) were found for both membranes.

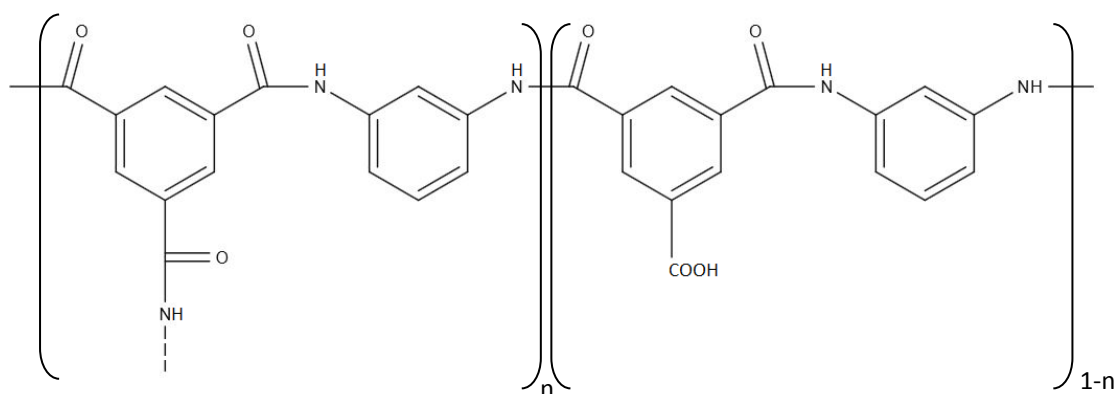


Figure 4.5. Chemical structure of a fully aromatic polyamide [44].

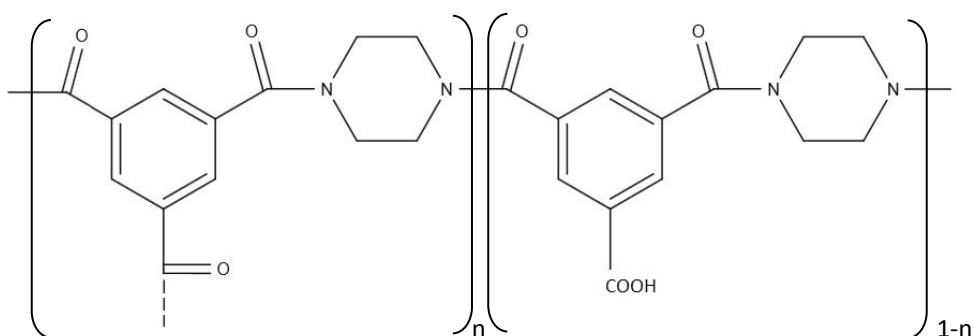


Figure 4.6. Chemical structure of a semi-aromatic polyamide (poly(piperazine)amide) [44].

Furthermore, bands due to methyl groups bending and SO_2 stretching were found (see Figure 4.4), which are characteristic for polysulfone (see Figure 4.7). The support layer of the NF99HF and UTC-60 is made from polysulfone and thus, bands can be found in the ATR-FTIR spectra because the penetration depth of the infrared spectrometer ($<200 \text{ nm}$ – $1 \text{ }\mu\text{m}$ [44,63]) complies to the thickness of the active layer ($\leq 1 \text{ }\mu\text{m}$ [2]).

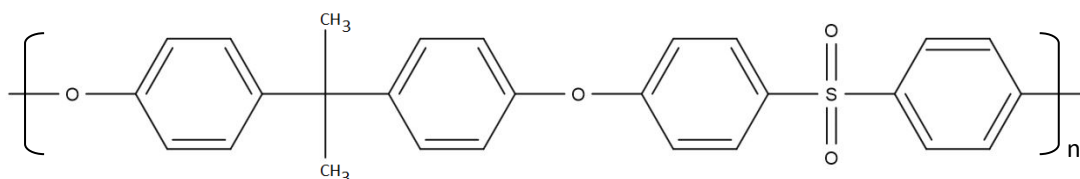


Figure 4.7. Chemical structure of polysulfone [62].

The thickness of the active polyamide surface layer was determined with SEM but can also be approximated by the ratio of the amide I band ($\sim 1626 \text{ cm}^{-1}$) to the aromatic band of the polysulfone layer ($\sim 1585 \text{ cm}^{-1}$) [62]. The ratio of the NF99HF (0.06) is slightly lower compared to the UTC-60 (0.08) and thus, the thickness of the active layer should be marginally thinner. This was also observed in SEM analysis and thus, the permeability of the NF99HF should be slightly enhanced compared to the UTC-60 because the permeability is proportional to the active surface thickness [14].

4.3.5 Zeta Potential

The zeta potential of the utilized membranes was determined with 1 mM NaCl , 1 mM MgSO_4 , and the synthetic feed solution (see Table 4.2) in a pH range between 2 and 5 (see Figure 4.8). Higher pH values were not streamed due to the fact that hydroxide precipitation would affect the measurements with the synthetic feed solution negatively.

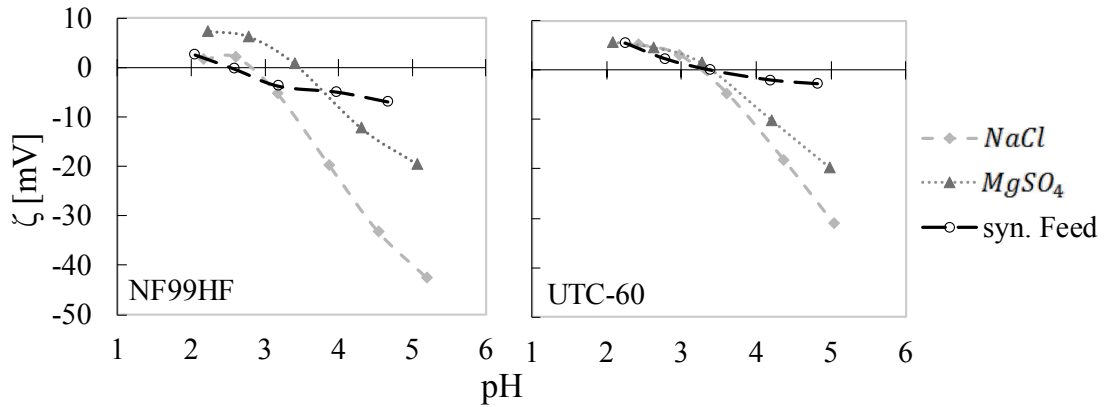


Figure 4.8. Zeta potential ζ in dependence of pH and utilized solution for the NF99HF and UTC-60.

As shown in Figure 4.8, the pH-dependent zeta potential curves of the membranes are quite similar below the isoelectric point, especially for the UTC-60 and the membrane surface is slightly positively charged. Moreover, the amphoteric character of the membrane surface, evoked by the functional groups (amine and carboxyl groups), which were detected by FTIR, is clearly visible. The IEP of the UTC-60 was determined at pH 3.3 for all tested solutions as shown in Figure 4.8. Richards et al. (2010) determined the IEP at pH 3.2 with 20 mM NaCl + 1 mM NaHCO_3 [37]. For the NF99HF, the IEP varies in dependence of the utilized solution and was determined at pH 2.9 for NaCl and the synthetic feed solution and at pH 3.5 for MgSO_4 . In the literature an IEP between pH 4.1–4.4 is reported for NF99HF, which was determined with 0.01 M NaCl [35]. However, the ionic strength of the utilized synthetic leaching solution seems responsible for the difference of the location of the measured IEP and the literature data. Different studies report that the IEP as well as the zeta potential progression can vary in dependence of the present ionic species and ionic strength [64,65].

For both membranes, the lowest zeta potential was observed with NaCl (pH 5: NF99HF ≤ -40 mV, UTC-60 ≤ -30 mV). Oatley et al. (2012) measured a similar progression for the NF99HF with 0.01 M NaCl [35]. If divalent ions are added to the solution, the zeta potential becomes less negative for MgSO_4 . For the synthetic feed solution, an increased zeta potential at pH 5 (NF99HF ≤ -8 mV, UTC-60 ≤ -5 mV) was determined. The membrane surface charge is shielded with increasing ionic strength of the solution and thus, the membrane is less negatively charged and repulsion effects are less pronounced [65].

4.3.6 Flux and Permeability

The flux of the utilized membranes was measured with deionized water as well as with 1 mM NaCl and 1 mM MgSO_4 (see Figure 4.9). The aim was to investigate how the presence of mono- and divalent ions affect the membrane performance. Moreover, the pH of the solution was adjusted with 1 M H_2SO_4 to pH 2 to examine if the acidic, sulfate-rich conditions have an influence on flux.

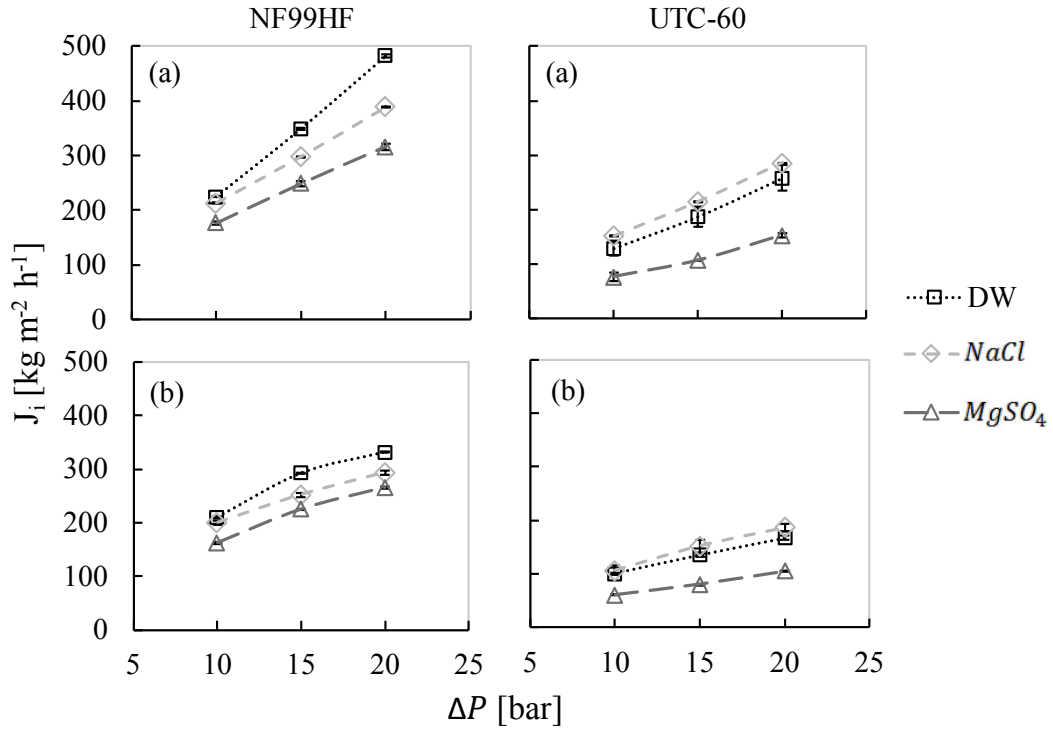


Figure 4.9. Flux J_i of the NF99HF and UTC-60 in dependence of transmembrane pressure (ΔP) determined with deionized water (DW), 1 mM NaCl and 1 mM MgSO_4 in cross-flow set-up (TMP: 15 bar, T : 25°C, v : 0.5 m s⁻¹) (a) without pH adjustment, (b) pH: 2.

As shown in Figure 4.9, the flux is enhanced in case the transmembrane pressure increases. Moreover, the flux of the NF99HF is higher compared to the UTC-60 as predicted in the AFM and contact angle measurements due to the smoother and hydrophilic membrane surface of the NF99HF. For both membranes, the MgSO_4 flux achieved the lowest values. The highest flux was measured for the NF99HF with deionized water and for the UTC-60 with NaCl . Moreover, the flux achieves lower values in case a pH of 2 is adjusted. Due to the increased ionic strength of the solution, mainly evoked by the addition of H_2SO_4 , the osmotic pressure is increased and thus, flux is declining. Nevertheless, the concentration polarization seems minimal for the conducted experiments because the flux increases linear with the transmembrane pressure and thus, the flux is still pressure controlled [66].

The permeability of the membranes is shown in Table 4.6 and it was observed that the NF99HF achieves higher values for deionized water compared to the literature. For the UTC-60, the pure water permeability is in the same range as reported.

Table 4.6. Permeability L_p of the NF99HF and UTC-60 for deionized water (DW), 1 mM NaCl, and 1 mM $MgSO_4$.

Feed solution	L_p [kg m ⁻² h ⁻¹ bar ⁻¹]			
	NF99HF		UTC-60	
	–	pH 2	–	pH 2
DW	23.5 ± 0.1	18.5 ± 0.1	12.8 ± 1.2	8.9 ± 0.2
	9–18 ^{a)}	n. a.	10 ^{b)} –15 ^{c)}	n. a.
NaCl	20.0 ± 0.1	16.6 ± 0.3	14.5 ± 0.1	9.9 ± 0.6
$MgSO_4$	16.5 ± 0.3	14.5 ± 0.1	7.2 ± 0.3	5.5 ± 0.1

n. a. – not available

^{a)}[36], ^{b)}[39], ^{c)}[40]

It is conspicuous that the permeability of the UTC-60 measured with $MgSO_4$ is only half as high as with NaCl (see Table 4.6). This drop is less significant for the NF99HF. This behavior might be explained by the surface charge of the membranes. Under neutral conditions, the zeta potential of the membranes is negative and SO_4^{2-} is repulsed more effective than Cl^- . Moreover, the hydrated radius of SO_4^{2-} (respectively Mg^{2+}) is enhanced [55] and thus, the steric hindrance increased and the permeability of $MgSO_4$ decreased.

At pH 2, the permeability is decreased compared to the neutral conditions. This time, the cations (Na^+ , Mg^{2+}) are repulsed from the positively charged membrane surface. Mg^{2+} is repulsed more effective due to the divalent charge. Moreover, the hydrated radius of Mg^{2+} is larger compared to SO_4^{2-} [55] and thus, the steric hindrance enhanced. Furthermore, the ionic strength of the feed solution is increased due to the addition of SO_4^{2-} as consequence of pH adjustment and thus, the osmotic pressure increased and the flux decreased.

However, taking the pure water flux into consideration, the effective membrane thickness over porosity $\Delta x/A_k$ can be estimated according to Eq. 2 [1,21,22]. The pore radius of the NF99HF is reported between 0.43 nm [35] and 0.46 nm [57]. Data about the pore radius of the UTC-60 is lacking. For the NF99HF, the ratio between Δx and A_k is approximately between 1.11 and 1.26 μm and corresponds to literature data for NF membranes with an equivalent pore radius and permeability [22]. The higher the ratio between $\Delta x/A_k$, the more freely the solute can permeate [1].

4.3.7 NaCl and MgSO₄ Retention

The retention of *NaCl* and *MgSO₄* is shown in Figure 4.10. Moreover, the influence of pH adjustment (pH 2) was investigated.

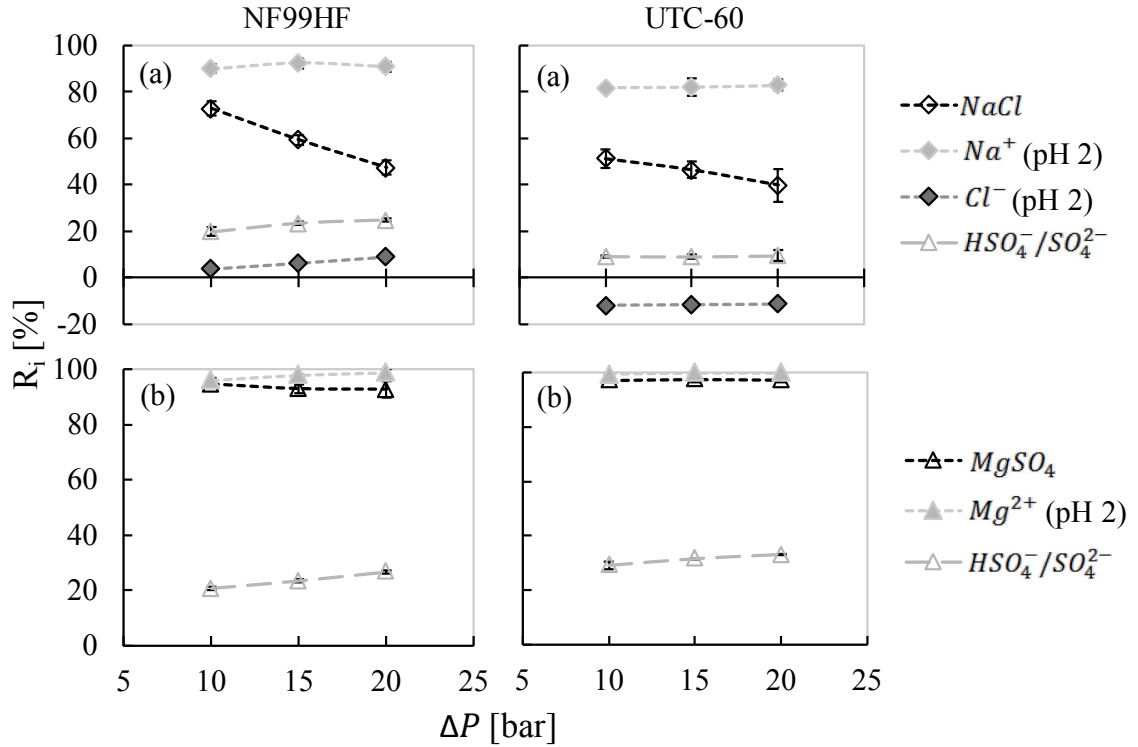


Figure 4.10. Retention R_i of the NF99HF and UTC-60 in dependence of transmembrane pressure ΔP determined with (a) 1 mM *NaCl*, (b) 1 mM *MgSO₄* in cross-flow set-up (TMP: 15 bar, T : 25°C, v : 0.5 m s⁻¹) with (pH 2) and without pH adjustment.

The mean *NaCl* retention of the NF99HF ($59.8 \pm 13.5\%$) is enhanced in comparison to the UTC-60 ($45.9 \pm 4.9\%$), which corresponds to the literature data from Table 4.1. Characteristics of the utilized NF membranes taken from the literature. Unmarked information was provided by the manufacturer. However, the obtained retention of the NF99HF, especially at 15 and 20 bar, is lower than predicted but Madsen et al. (2014) also reported comparatively low Na^+ (53.0%) and Cl^- (41.3%) retentions [58]. The decrease of the *NaCl* retention in dependence of the transmembrane pressure was observed for both membranes. As shown in Figure 4.9, the flux is enhanced in case the transmembrane pressure increases and thus, the retention should be enhanced, too [67,68]. However, for low *NaCl* concentrations and a low flow velocity Koyuncu and Topacik (2003) observed that the salt retention is decreasing while the transmembrane pressure is increasing. An explanation might be that the solvent and solute flux is increased due to the enhanced transmembrane pressure [69].

Under neutral conditions Na^+ with a hydrated radius r_h of 0.385 nm [55] is mainly rejected by size and Cl^- ($r_h = 0.332$ nm [55]) achieves the same retentions mainly based on dielectric exclusion and charge balancing. Nevertheless, the retention of Na^+ and Cl^- is not equal anymore in case the pH is adjusted to pH 2. As shown in Figure 4.10(a), the Na^+ retention is increased because the ions are additionally repulsed from the positively charged membrane surface. In comparison, the Cl^- retention is strongly decreased due to the presence of HSO_4^-/SO_4^{2-} , which are both present at pH 2 after H_2SO_4 dissociation [70]. The partitioning of the mono- and divalent anions is a consequence of steric hindrance and the Donnan effect. The hydrated radius of SO_4^{2-} ($r_h = 0.379$ nm [55]) and HSO_4^- is larger compared to Cl^- and thus, the HSO_4^-/SO_4^{2-} retention is enhanced due to steric hindrance. A dielectric exclusion can be ruled out as the membrane surface charge is slightly positive and thus attraction mechanisms are more pronounced. Moreover, the Cl^- permeation is increased (respectively the retention is decreased) because the divalent negative charge of SO_4^{2-} needs to be balanced to establish the Donnan equilibrium. As consequence, the retention can even achieve negative values as for the UTC-60 (see Figure 4.10(a)).

Due to the enlarged solute radius of SO_4^{2-} , the retention typically achieves values $>80\%$ but with increasing H_2SO_4 concentration, the SO_4^{2-} retention is rapidly decreasing [71]. Moreover, the retention of the smaller monovalent specie HSO_4^- , which is dominating at pH 2 [70], led to the comparatively low retention because it is less rejected. Next to pH, the fraction of H_2SO_4 is a function of the H_2SO_4 concentration [71]. The total SO_4^{2-} concentration was measured by ion chromatography and achieved values of approx. 1000 mg L^{-1} . Visser et al. (2001) reported retentions of 40% at pH 1.9 with comparable NF membranes and SO_4^{2-} concentrations [71].

The $MgSO_4$ retention (see Figure 4.10(b)), NF99HF: $93.3 \pm 1.2\%$, UTC-60: $97.3 \pm 0.1\%$) corresponds with the literature data from Table 4.1. Mg^{2+} ($r_h = 0.428$ nm [55]) is mainly rejected by size. Under neutral conditions SO_4^{2-} is dominant [70] and achieves the same retentions like Mg^{2+} due to dielectric exclusion and charge balancing. Under acidic, sulfate-rich conditions, the Mg^{2+} retention is slightly increased as a result of repulsion (NF99HF: $97.6 \pm 0.3\%$, UTC-60: $99.7 \pm 0.2\%$) and the HSO_4^-/SO_4^{2-} retention achieves nearly the same values as in the experiment with $NaCl$.

4.3.8 Separation Performance of Strategic Elements

To evaluate the separation performance of the utilized membranes, the flux was compared to the deionized water flux (see Figure 4.11) and the retention of the synthetic feed solution with different strategic elements included was determined (see Figure 4.12).

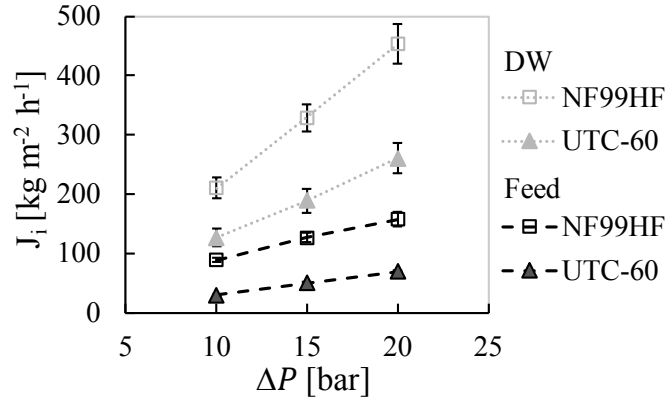


Figure 4.11. Flux J_i of the NF99HF and UTC-60 in dependence of transmembrane pressure (ΔP) determined with the synthetic feed solution in cross-flow set-up (TMP: 15 bar, T : 25°C, v : 0.5 m s⁻¹) in comparison to the deionized water (DW) flux.

Similar to the experiments with deionized water, the flux is enhanced with increasing transmembrane pressure. However, the flux of the NF99HF is decreased by a factor of 1.6–2.9 and for the UTC-60 by 3.7–4.2 in case the synthetic feed solution is treated. The ionic strength of the solution is strongly enhanced. Hence, the osmotic pressure is increased and the flux declined. Moreover, a high concentration of divalent cations (Co^{2+} , Cu^{2+} , Zn^{2+}) is included and their retention tend to be very high (see Figure 4.12). Therefore, the permeability is significantly decreased (NF99HF: 8.4 ± 0.6 kg m⁻² h⁻¹ bar⁻¹, UTC-60: 3.3 ± 0.1 kg m⁻² h⁻¹ bar⁻¹) compared to $NaCl$ and $MgSO_4$ (see Table 4.6).

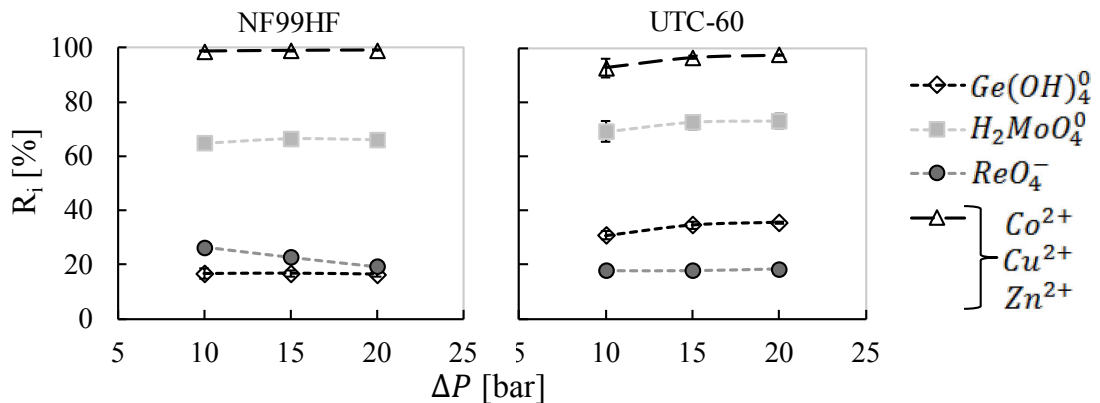


Figure 4.12. Retention R_i of the (a) NF99HF and (b) UTC-60 in dependence of transmembrane pressure (ΔP) determined with the synthetic feed solution (pH 2) in cross-flow set-up (TMP: 15 bar, T : 25°C, v : 0.5 m s⁻¹).

As shown in Figure 4.12, the cations (Co^{2+} , Cu^{2+} , Zn^{2+}) achieve retentions $\geq 91\%$ for both membranes and meet the values of Mg^{2+} . Similar to the experiments with $MgSO_4$, the divalent cations are rejected by size (see Table 4.2) and additionally repulsed from the positive membrane surface.

The perrhenate (ReO_4^-) retentions are higher than for Cl^- at pH 2 (see Figure 4.10), which can be explained by the addition of the chemical compounds $CoSO_4$, $CuSO_4$ but mainly $ZnSO_4$. Meschke et al. (2017) showed that ReO_4^- can achieve retentions $\leq 0\%$ at pH 2 for the utilized membranes in case the cations are excluded [34], which is quite similar to the results of Cl^- . Nevertheless, with increasing cation and SO_4^{2-} concentration, the Re retention increases to 20–30%. It can be assumed that the Re permeation is impeded by the increased polarization layer. Moreover, the increased cation concentration needs to be balanced. It seems likely that the positive membrane surface charge is shielded by the SO_4^{2-} ions as shown in the streaming potential measurements (see Figure 4.8) and thus, ReO_4^- is less attracted. Furthermore, it has to be considered that with increasing acidity, the HSO_4^- species is dominating and SO_4^{2-} is less present [70]. The HSO_4^- ions are less hydrated [72,73] and consequently in stronger permeation competition with the Re ions. Therefore, the Re retention may be increased, too.

The retention of uncharged solute differs slightly for Mo but significantly for Ge for the utilized membranes. Considering the enhanced Ge retention of the UTC-60 it can be assumed that the MWCO is smaller and thus, the retention increased. Nevertheless, the results are not consistent regarding the $NaCl$ experiments and indicate that the pore size distribution of the UTC-60 is subject to a certain variation.

The reflection coefficient of uncharged solutes can be estimated according to Eq. 1. The radius of uncharged solutes r_s can be approximated after Eq. 11 [74] taking the molecular weight MW into consideration.

$$r_s = \frac{0.065 \cdot MW^{0.438}}{2} \quad (11)$$

The ratio between the solute radius and pore radius can be expressed by λ . Bowen et al. (1997) reported about the relationship between $\Delta x/A_k$ and λ , which is shown in Eq. 12 [1].

$$\Delta x/A_k = 3.09e^{-1.95\lambda} \quad (12)$$

Table 4.7 shows the approximated solute radius of the uncharged solutes *Ge* and *Mo* and their estimated reflection coefficients for the NF99HF. Moreover, the effective membrane thickness over porosity was calculated.

Table 4.7. Estimated solute radius r_s , reflection coefficient σ , and $\Delta x/A_k$ of $Ge(OH)_4^0$ and $H_2MoO_4^0$ for the NF99HF.

Species	MW [g mol ⁻¹]	r_s [nm]	σ [%]	$\Delta x/A_k$ [μm]
$Ge(OH)_4^0$	140.7	0.206*	29.9–34.0	1.21–1.29
		0.284**	54.5–61.4	
$H_2MoO_4^0$	162.0	0.247*	42.1–47.7	1.01–1.08
		0.302**	60.8–68.2	

* MolView [54], **Eq. 11

As shown in Table 4.7, the reflection coefficient calculated with the solutes radius from Eq. 11 seems overestimated for *Ge* but fits very well for *Mo*. The *Ge* radius, which was determined by steric confirmation of the solute lies closer to the experimental data. However, the estimation does not consider mutual interferences evoked by the multicomponent solution.

The ratio of $\Delta x/A_k$ is increased for $Ge(OH)_4^0$ compared to $H_2MoO_4^0$ (see Table 4.7). The same correlation was reported by Bowen et al. (1997) for neutral solutes. In comparison to large solutes, the smaller solutes can permeate more freely and thus $\Delta x/A_k$ is enhanced [1]. The same applies for the charged feed components like *Re* (ReO_4^-). Due to the smaller hydrated radius in comparison to the cations (see Table 4.2), the permeation is enhanced because steric hindrance is less pronounced. Moreover, the membrane surface is slightly positively charged at pH 2 and attraction mechanisms intensify permeation.

However, the separation performance of charged solutes is not only affected by size and dielectric exclusion as the diffusive transport has to be considered as well. The contribution of diffusion is strongly enhanced compared to convection and electromigration [68,75]. In case the pore radius becomes smaller, the diffusion is substantially enhanced [68]. Taking the diffusion coefficients of the anions into consideration (see Table 4.8), the lower Cl^- retention at pH 2 in comparison to ReO_4^- can be explained by the enhanced diffusivity of Cl^- .

Table 4.8. Diffusion coefficients D_i in aqueous solution at infinite dilution [76].

Species	D_i [$10^{-9} \text{ m}^2 \text{ s}^{-1}$]	Species	D_i [$10^{-9} \text{ m}^2 \text{ s}^{-1}$]
Na^+	1.334	ReO_4^-	1.462
Cl^-	2.032	Co^{2+}	0.732
Mg^{2+}	0.706	Cu^{2+}	0.714
SO_4^{2-}	1.065	Zn^{2+}	0.703

As shown in Table 4.8, the diffusion coefficient of ReO_4^- and Na^+ are in the same range, but Na^+ has a higher hydrated radius and, in addition is repulsed by the positively charged membrane surface at pH 2. Thus, retentions are contrary. The diffusivity of the divalent cations is almost equal and it can be concluded that the retention should decrease in the order $\text{Zn} > \text{Cu} > \text{Co}$, which can be confirmed by the retentions of the UTC-60 (10 bar: 96.7% $\text{Zn}^{2+} > 91.3\% \text{ Cu}^{2+} > 90.5\% \text{ Co}^{2+}$). Nevertheless, the cation retention is mainly the result of size exclusion and should decrease in the order $\text{Zn} > \text{Co} > \text{Cu}$ (see Table 4.2), which was observed for the NF99HF (10 bar: 98.8% $\text{Zn}^{2+} = 98.8\% \text{ Co}^{2+} > 98.4\% \text{ Cu}^{2+}$).

Considering everything, experiments conclude that *Ge* and *Re* can be separated from *Co*, *Cu*, and *Zn* best with the NF99HF, which also has the higher permeability. The membrane could be used for pre-fractionation to reduce energy consumption in subsequent processes like reverse osmosis to concentrate e.g. *Re*. Nevertheless, further investigations focus on the increase of selectivity by varying different process parameters like flow velocity and temperature.

4.4 Conclusion

The membrane characterization was conducted by AFM, SEM, FTIR, contact angle, and streaming potential measurements. The results show that the NF99HF is smoother and more hydrophilic than the UTC-60 but the thickness of the active layer tends to be equal. As consequence, the permeability of the UTC-60 was significantly decreased but the separation performance was almost equal compared to the NF99HF. The main difference was observed with *NaCl* and the addition of H_2SO_4 to adjust a pH of 2. The Donnan effect was enhanced for the UTC-60 and thus, Cl^- achieved considerably lower retentions.

The experimental results indicate that divalent cations are mainly rejected by size, independently of pH. For monovalent cations size exclusion is less pronounced due to the smaller hydrated radius. As a consequence, the retention was decreased in comparison to

the divalent cations. Moreover, repulsion effects at pH 2 are more pronounced for monovalent cations and thus, the retention was increased.

The retention of monovalent anions like ReO_4^- can be influenced by the addition of divalent ions and the variation of the membrane surface charge by changing the pH. Therefore, further investigations shall be conducted at higher pH values and varying concentrations of e.g. SO_4^{2-} .

Currently, both utilized NF membranes (NF99HF, UTC-60) show a good separation selectivity towards *Re* and *Ge* but the separation efficiency shall be enhanced. The influence of the transmembrane pressure was negligible and further investigations should determine if e.g. higher flow velocities may affect the separation performance positively. This might have an influence on the uncharged solutes because their retention is mainly controlled by the diffusive and convective flow.

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5. Influence of Process Parameters

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Influence of process parameters on separation performance of strategic elements by polymeric nanofiltration membranes

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Abstract

Employing nanofiltration, a separation of uncharged solutes, monovalent, and bivalent ions from multicomponent aqueous solutions is potentially feasible. Separation is strongly influenced by process parameters as well as the feed properties and membrane characteristics. The aqueous solution in this study includes strategic elements (*Ge*, *Co*, *Mo*, *Re*) in a wide range of concentrations and varying ionic species. The feed composition mirrors a bioleachate of a German flue dust resulting from copper ore smelting. In a number of cross-flow experiments, the separation performance of eight commercial polymeric nanofiltration membranes was evaluated and the influence of transmembrane pressure, flow velocity, flow regime, recovery, and ionic strength was investigated. It was observed that a high ionic strength (evoked by a high *Zn* concentration) affects *Re* retention negatively and decreases permeability. By increasing the transmembrane pressure, the separation selectivity towards *Re* is enhanced. An almost quantitative *Re* separation is realized with a cut-off below 200 Da (RO90, NE-90). The utilized NF99HF membrane shows the best results regarding permeability and separation selectivity towards *Re*, *Ge*, and *Mo*.

5.1 Introduction

The global demand of raw materials such as strategic elements is increasing [1–3] and secondary resources are garnering increasing attention [4–6]. Processes such as urban mining, landfill mining or secondary mining, aim at recovering and/or recycling previously unutilized raw materials [7–9]. This study focuses on a deposited flue dust from German copper ore smelting rich in various strategic elements (e.g. *Ag*, *Co*, *Cu*, *Ge*, *Mo*, *Re*, *Sn*, *Zn*) [10], which partly have a high economic relevance for the European Union due to supply dependencies [11] and shall be mobilized by bioleaching [12]. The elements downstream processes such as solvent extraction, anion exchange, and nanofiltration (NF) are investigated for separation and concentration of the dissolved strategic elements [13].

NF is a promising membrane technique for the envisioned separation task as mono- ($R_i < 50\%$) and bivalent ions ($R_i > 90\%$) as well as uncharged solute are separated by size exclusion, dielectric exclusion, solution diffusion, and adsorption mechanisms [14,15]. NF membranes show characteristics of ultrafiltration (steric hindrance) and reverse osmosis (solution-diffusion) membranes [14,16]. Thin film composite NF membranes with a polyamide active surface layer are frequently utilized [14]. Their separation performance mainly depends on membrane characteristics (e.g. thickness of active layer, pore size, membrane charge), process parameters (e.g. temperature, transmembrane pressure, fluid dynamic conditions), and feed properties (e.g. pH, concentration, ionic strength, ionic speciation) [15,17,18].

For example, a high temperature may result in a changed membrane structure [17,19,20] because the polymers may be reorientated [20–22]. The resulting polymer structure is less dense [21,22] and thus, flux is increased and retention decreased until a critical temperature is exceeded [19,21]. Moreover, the membranes can become more sensitive to the influence of transmembrane pressure and pH in case of high operation temperature [17]. Due to the fact that bioleaching is conducted under controlled conditions, the temperature of the leachate is almost constant [12].

The pH exerts a major influence on the ionic speciation of solutes, resulting in an effect on membrane charge and thus, the membrane is positively charged below the isoelectric point (IEP) and negative charged above it [23]. The IEP of most polymeric nanofiltration membranes is between pH 3–6 [15,18,23]. Therefore, electrostatic repulsion or attraction mechanisms between charged membrane surface and charged solute can occur above or

below the IEP [15,23]. Due to the fact that carboxyl groups are located on the polyamide surface, which can be dissociated, the repulsion is even more pronounced [15,23]. Here, the utilized feed solution, which is referred to a controlled bioleaching process, is acidic (approx. pH 2) and pH almost constant [12]. At pH 2, the surface charge of the utilized membranes is slightly positive, which was confirmed in our previous study [24]. In acidic conditions, all target elements (*Ge*, *Mo*, *Re*, *Co*, *Cu*, *Zn*) remain as ions in the solution but their net charge (negative, positive, and neutral) varies. Jia et al. (2019) reported that divalent heavy metal ions (e.g. Cd^{2+} , Ni^{2+}) can be retained >93% in an acid pH range by polymeric thin-film composite membranes [25]. Nevertheless, own prior work confirms that pH has a significant influence on retention [26,27] but pH adjustment is currently uneconomical and precipitation as well as coprecipitation occurs due to the high amount of *Zn* (and *Fe*) in the bioleaching solution [12]. Hence, the influence of pH was not studied any further.

Moreover, membrane swelling is pH-, temperature-, and salt concentration-dependent [17,19,28] and thus, the thickness of the active layer as well as the pore size is affected [20,28–30]. It needs to be considered that the permeation rate is proportional to the active layer thickness, which is typically $\leq 1 \mu m$ for NF membranes [14,31]. The main components of the leaching solution with approx. 3000 mg L⁻¹ each are *Zn* and *S* [12] and thus, the solution as a high ionic strength, which has a major effect on membrane performance [20,28]. By a tangential cross-flow velocity and a turbulent flow regime induced by a spacer as turbulence promoter, the shear stress over the membrane can be enhanced and thus, occurring concentration polarization and fouling can be decreased [14,32–34].

The present study aimed at investigating to identify appropriate NF process conditions to separate the focused strategic elements (*Co*, *Ge*, *Mo*, *Re*) from the multicomponent leaching solution for a potential technical scale-up. Moreover, a preconcentration would be desirable, so that envisioned conducted downstream processes such as solvent extraction or adsorption [13] become more worthwhile. Therefore, the flow velocity, flow regime, transmembrane pressure, recovery, and ionic strength (varying *Zn* concentration) were studied. Eight polymeric NF membranes (NF99HF, NF, RO90, UTC-60, NE-70, NE-90, NF345HP, and NP010) were screened to evaluate their separation performance towards strategic elements. Currently, a separation cannot be realized by any downstream process. The NF is not meant to separate and concentrate independently but as a part of a

purposed downstream process in combination with other separation techniques such as solvent extraction and reverse osmosis.

5.2 Materials and Methods

5.2.1 Nanofiltration Membranes

In the study presented, the performance of eight commercial polymeric nanofiltration membranes (see Table 5.1) was evaluated in terms of retention, flux and permeability. The membranes were chosen on the basis of previous investigations [24,26,27] due to high selectivity, chemical resistance, and pure water permeability. The retention R_i is represented by the ratio of the ion concentration c_i of the permeate to those of the feed and can be calculated according to Eq. 1.

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

The flux J_i (see Eq. 2) can be expressed by the mass flow of the permeate $\dot{m}_p$, which is collected by unit membrane area A .

$$J_i [kg \, m^{-2} \, h^{-1}] = \frac{\dot{m}_p}{A} \quad (2)$$

Taking the applied transmembrane pressure TMP into consideration, the permeability L_p of the tested membranes can be expressed by Eq. 3.

$$L_p [kg \, m^{-2} \, h^{-1} \, bar^{-1}] = \frac{\dot{m}_p}{A \cdot TMP} \quad (3)$$

Table 5.1. Main characteristics of the utilized thin-film composite nanofiltration membranes. Unmarked information was provided by the manufacturer.

Characteristic	Membrane							
	NF99HF	NF (NF99, NFT-50)	RO90 (NF97)	UTC-60	NE-70	NE-90	NF345HP	NP010*
Manufacturer	Alfa Laval AB	Alfa Laval AB	Alfa Laval AB	CSM [®] (Toray Ind. Inc.)	CSM [®] (Toray Ind. Inc.)	CSM [®] (Toray Ind. Inc.)	Dow Filmtec [™]	Microdyn-Nadir GmbH
Active layer	PA	PPA ^{c)i)}	PA	PPA	PPA	PA	PPA	PES
MWCO [Da]	≥200	≥200	≤200	150–300	250	200	200	1000
T_{max} [°C]	50	50	50	45	45	45	45	95
p_{max} [bar]	55	55	55	41	41.4	41.4	41	40
pH range [–]	3–10	3–10	3–10	3–8	2–11	2–11	2–11	0–14
IEP [pH]	4.1–4.4 ^{a)}	4.3 ^{c)} 4.2 ± 0.2 ⁱ⁾	4.1 ^{d)}	3.2 ^{a)}	n. a.	5 ^{j)}	n. a.	3–4 ^{g)h)}
R_i [%] <i>NaCl</i>	72 ^{b)}	76 ^{b)}	≥90	30 ^{k)} – 55	≥40	≥85	n. a.	10
R_i [%] <i>MgSO₄</i>	≥98	≥98	≥97	≥97	≥97	≥97	≥98.5	25–55 ^{b)}
$L_P^\dagger$ [kg m ⁻² h ⁻¹ bar ⁻¹]	9–18 ^{b)}	5.9 ⁱ⁾ –10 ^{b)}	1–6 ^{b)}	10 ^{e)} –15 ^{f)}	n. a.	n. a.	n. a.	11–30 ^{b)}

*Flat sheet membrane

[†]pure water

PA – Polyamide, PPA – Poly(piperazine)amide, PES – Polyethersulfone

n. a. – not available

^{a)}[35], ^{b)}[36], ^{c)}[17], ^{d)}[37], ^{e)}[38], ^{f)}[39], ^{g)}[40], ^{h)}[41], ⁱ⁾[42], ^{j)}[43], ^{k)}[44]

5.2.2 Synthetic Feed Solution

To evaluate the separation performance of the NF membranes a synthetic feed solution (model solution) was used, which contained the elements *Mo*, *Ge*, *Re*, *Co*, *Cu*, and *Zn* in a wide range of concentration (see Table 5.2). The chosen feed composition is a reference to a bioleaching process of a flue dust (Theisen sludge) from German copper ore smelting [10,12]. The pH of the feed was adjusted with 1 M H_2SO_4 to pH 2 as the bioleaching solution is acidic (pH 2–3) and sulfate-rich (approx. 3000 mg S L⁻¹) [12]. By ICP-MS (Agilent Technologies Inc., 7700 Series), the *Ge*, *Re*, *Mo*, and *Co* concentrations were measured. ICP-AES (Spectro Analytical Instruments GmbH, Ciros) was used for *Cu* and *Zn* as consequence of the expected higher concentration.

Table 5.2. Main characteristics of the synthetic feed solution used in this study.

Element	$c_{i,F}$ [mg L ⁻¹]	Chemical compound	Purity [%]	Manu- facturer	Ionic species [pH 2]	r_h [nm]
<i>Mo</i>	0.5	Sodium molybdate(VI) dihydrate	98.0	Alfa Aesar	$H_2MoO_4^{0a)}$	0.247 ^{g)}
<i>Ge</i>	1.0	Germanium(IV) dioxide	99.999	Alfa Aesar	$Ge(OH)_4^{0b)}$	0.206 ^{g)}
<i>Re</i>	1.0	Sodium perrhenate(VII)	99+	Alfa Aesar	$ReO_4^{-c)}$	0.352 ^{h)}
<i>Co</i>	2.0	Cobalt(II) sulfate heptahydrate	99+	AnalaR Normapur	$Co^{2+d)}$	0.423 ^{h)}
<i>Cu</i>	100	Copper(II) sulfate	≥99.0	Sigma Aldrich	$Cu^{2+e)}$	0.419 ^{h)}
<i>Zn</i>	3000	Zinc(II) sulfate monohydrate	≥99.0	Sigma Aldrich	$Zn^{2+f)}$	0.430 ^{h)}

^{a)}[45], ^{b)}[46–48], ^{c)}[49], ^{d)}[60][50], ^{e)}[51], ^{f)}[52], ^{g)}[53], ^{h)}[54]

5.2.3 Experimental Cross-flow Set-up

The separation performance of the NF membranes was evaluated in cross-flow set-up, which is shown in Figure 5.1. The set-up includes two membrane modules, which are connected in parallel for double determination. Each module has an active surface area of 76 cm². Due to mechanical resistance, the membranes were installed upon sinter discs. By a piston diaphragm pump (Verder Deutschland GmbH & Co. KG, Typ G03), the feed (5 L) was transported and the transmembrane pressure ($TMP = 10\text{--}20$ bar, interval: 5 bar) was built up by a pressure reducer valve (Badger Meter Europa GmbH, Typ RC 200).

Transmembrane pressure and temperature ($T = 20^{\circ}\text{C}$) were kept constant during the experiments. Flow velocity ($v = 0.5\text{--}1.1 \text{ m s}^{-1}$, interval: 0.2 m s^{-1}) was adjusted by the pump's flow rate and controlled by a flow meter (Meister Strömungstechnik GmbH, Typ DHGA-10). The experiment was started after all process parameters (TMP , T , v) were constant (approx. 30 min). The permeate was led out pressureless and weighted on a precision scale (Kern & Sohn GmbH, Typ PCB 2500, readout: 0.01 g). At each operating point the recovery (see Eq. 4) was set to 1%. To evaluate the influence of recovery on separation performance, a recovery between 10 and 80% was tested (see Table 5.3).

$$\text{Recovery [\%]} = \frac{m_{p,t=\text{end}}}{m_{f,t=0}} \cdot 100\% \quad (4)$$

In addition, the Zn concentration was altered because it is the main component of the solutions and evokes the high ionic strength. The experimental design is shown in Table 5.3.

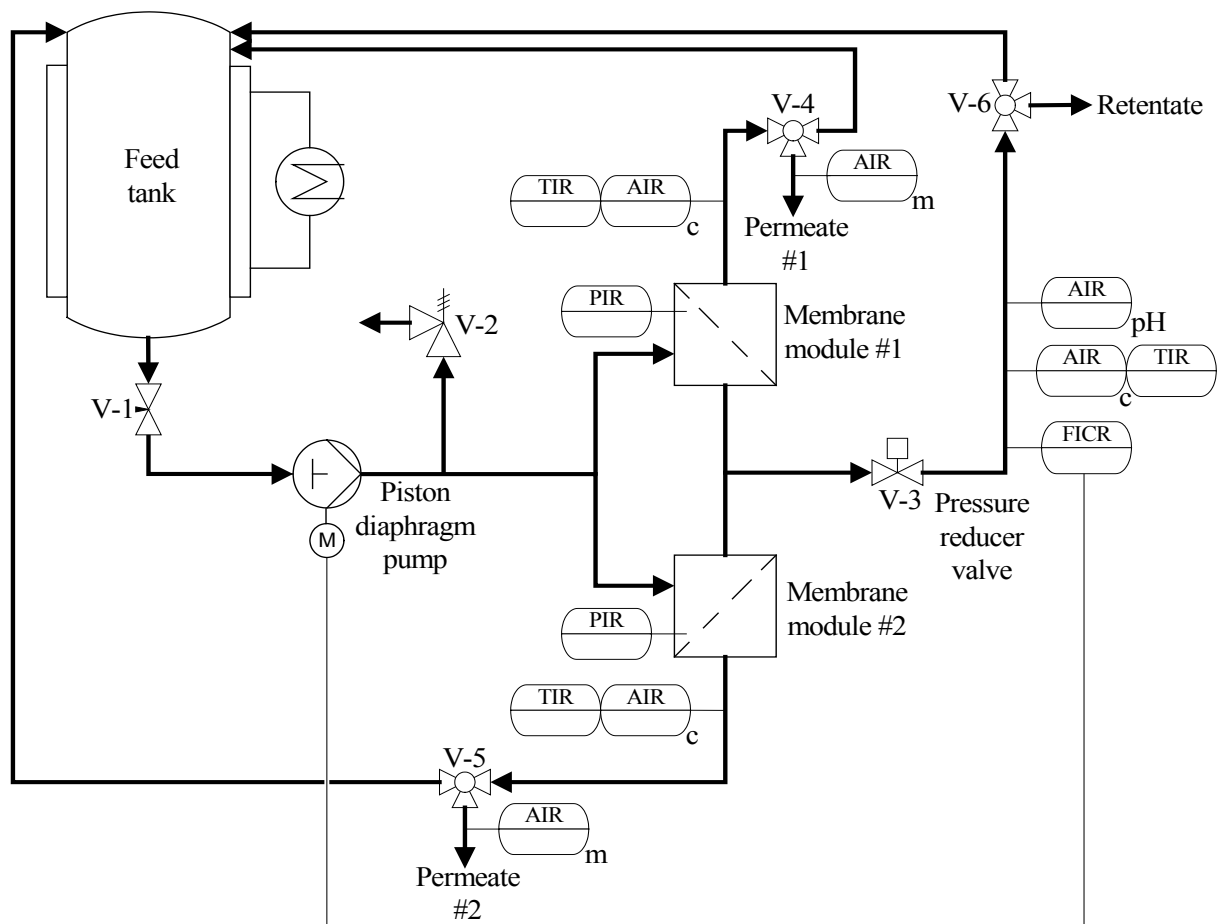


Figure 5.1. Schematic presentation of the cross-flow set-up (c – conductivity, m – mass).

Table 5.3. Experimental design.

Membrane	TMP [bar]	v [m s ⁻¹]	c_{Zn} [mg L ⁻¹]	Recovery [%]
NF99HF NF RO90 UTC-60 NE-70/-90 NF345HP NP010	15	0.5	3000	1
NF99HF	10 15 20	0.5–1.1	3000	1
	10 15 20	0.5	3000	
	10 15 20	0.5	100 1000 3000	
NF99HF RO90	15	0.5	3000	10–80

5.3 Results and Discussion

5.3.1 Retention and Permeability of the Utilized NF Membranes

The separation performance of eight commercial polymeric NF membranes was determined and compared with each other to investigate if it is possible to separate one or more strategic elements from the multicomponent solution by a high permeability. The determined retention of each element (*Ge*, *Mo*, *Re*, *Co*, *Cu*, *Zn*) is shown in Figure 5.2 and the permeability of each membrane in Figure 5.4.

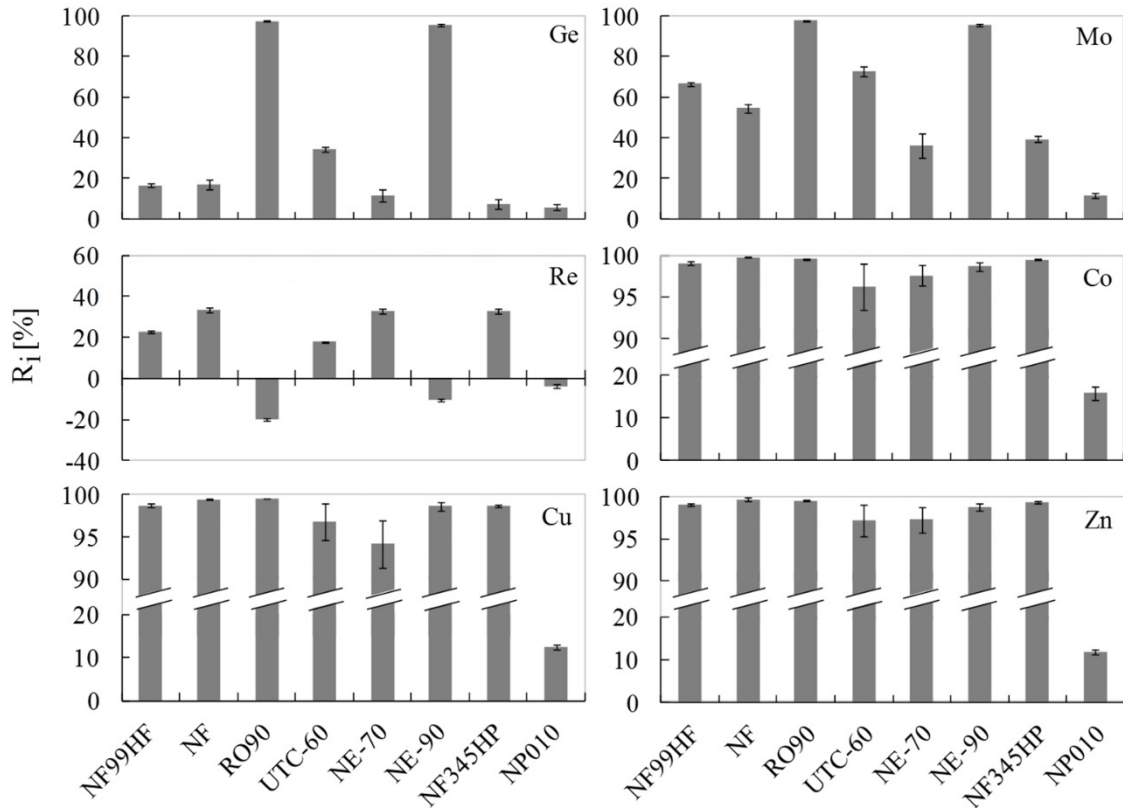


Figure 5.2. *Ge*, *Mo*, *Re*, *Co*, *Cu*, and *Zn* retention R_i of the utilized NF membranes for the synthetic feed with 3000 mg Zn L⁻¹ (TMP : 15 bar, T : 20°C, v : 0.5 m s⁻¹, pH : 2, recovery: 1%).

Ge and Mo retention

Under acidic conditions, *Ge* is present as $Ge(OH)_4^0$ and thus, the retention is mainly evoked by size exclusion. Literature data about the hydrated radius of Germanic acid is non-existent but the distance of the *Ge-O* bond is reported between 0.173 and 0.175 nm [55–57]. Meschke et al. (2017) estimated the radius of $Ge(OH)_4$ with 0.206 nm [27,53]. The *Ge* retention increases in the order NP010 ($\leq 7\%$) $\approx$ NF345HP < NE-70 < NF $\approx$ NF99HF < UTC-60 < NE-90 $\approx$ RO90 ($\geq 97\%$) and confirms that the membrane with the highest MWCO (NP010: 1000 Da) achieves the lowest and the membrane with the smallest MWCO (RO90 ≤ 200 Da) the highest retention (see Figure 5.2).

Similar to *Ge*, *Mo* is present as neutral solute ($H_2MoO_4^0$). The results indicate that *Mo* has a higher hydrated radius because the retention is enhanced compared to *Ge*. Meschke et al. (2017) estimated a radius of 0.247 nm for the neutral solute [27]. The retention increases nearly equivalently to *Ge* in the order NP010 ($\leq 13\%$) < NF345HP $\approx$ NE-70 < NF < NF99HF < UTC-60 < NE-90 $\approx$ RO90 ($\geq 98\%$), which fits quite well with the MWCOs (see Table 5.1). Nevertheless, the provided MWCO of the NE345HP (200 Da) seems underestimated as the results fits better to membranes with a larger cut-off such as the NE-70 (250 Da). It is assumed that the neutral solutes are only in competition with each other in the convective transport across the membrane. Other separation mechanisms such as diffusion and adsorption were not considered because convection dominates the diffusion [58].

As the separation of the uncharged elements *Ge* and *Mo* is mainly based on size exclusion, the MWCO or the pore size of the membranes is of enormous interest. Therefore, the *Ge/Mo* selectivity $S_{i,j}$ (see Eq. 5) was calculated taking the concentration of the elements (i, j) in the permeate (c_P) and retentate (c_R) into consideration to evaluate the relation between MWCO and *Mo/Ge* separation. The closer the selectivity to 1 (see Figure 5.3), the less selective is the separation between the *Ge* and *Mo*. A relatively high or a small cut-off is mainly responsible for this effect.

$$S_{i,j} = [-] = \frac{c_{P,i}/c_{P,j}}{c_{R,i}/c_{R,j}} \quad (5)$$

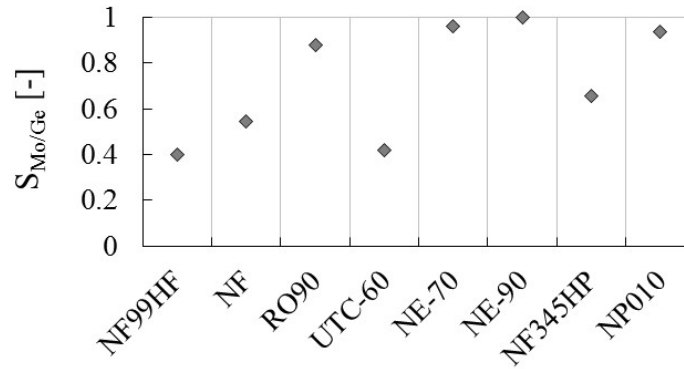


Figure 5.3. *Mo/Ge-Selectivity of the utilized NF membranes.*

As shown in Figure 5.3, the selectivity suggests that NF99HF and UTC-60 have nearly the same cut-off or respectively the same pore size, followed by NF and NF345HP. For NF99HF, a pore size of 0.430 nm can be found in the literature [35]. Moreover, NF99HF and UTC-60 show the best separation performance towards *Mo/Ge*. For NP010, the screened membrane with the highest cut-off, a pore size of 1.33 nm is recommended [59] and a separation of the uncharged components *Ge* and *Mo* is not feasible. RO90 and NE-90 are neither non-selective for a *Mo/Ge* separation due to the denser active layer.

Re retention

At pH 2, *Re* is present as perrhenate (ReO_4^-) and the retention increase in the order RO90 ($-19.8 \pm 0.3\%$) < NE-90 < NP010 < UTC-60 < NF99HF < NF $\approx$ NE-70 $\approx$ NF345HP ($32.9 \pm 1.6\%$), which is completely different to *Ge* and *Mo*. RO90 and NE-90, which achieved retentions $\geq 95\%$ for the uncharged solutes, showed negative *Re* retentions. This is explained by the Donnan effect. At pH 2, the feed solution contains a high amount of sulfate (SO_4^{2-}) and hydrogen sulfate (HSO_4^-) [60], which is mainly rejected by size. Therefore, the electroneutrality of the membrane needs to be established and thus, more *Re* permeates through the membrane, which is additionally attracted from the positively charged membrane surface at pH 2. In the case, the membrane surface is electroneutral due to charge shielding by the sulfate compounds, the negative rejection of *Re* may result by virtue of ion competing transport [61]. In comparison, for the more porous membranes NF99HF and UTC-60, Meschke et al. (2018) determined SO_4^{2-}/HSO_4^- retentions between 10–15% [24] and thus, electrostatic balancing is less pronounced and the *Re* retention increased. Nevertheless, with RO90 and NE-90 a separation of *Re* is feasible from the multicomponent leaching solution because all other elements are almost fully retained.

Co, Cu, and Zn retention

Under acidic conditions, the elements *Co*, *Cu*, and *Zn* are present as divalent cations and mainly rejected by size due to steric hindrance. Moreover, a little influence of dielectric exclusion can be assumed because the zeta potential of these membranes is slightly positive (see Table 5.1). The lowest retentions ($14.9 \pm 1.8\%$) is observed for NP010 due to the highest MWCO. All other membranes achieve retentions of $98.7 \pm 2.3\%$ on average. UTC-60 represents the minimum and RO90 the maximum.

Permeability

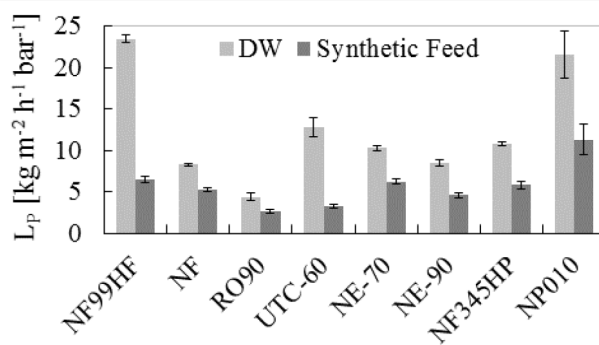


Figure 5.4. Permeability L_p of the utilized NF membranes measured with deionized water (DW) and synthetic feed with $3000 \text{ mg Zn L}^{-1}$ (TMP: 15 bar, T : 20°C , v : 0.5 m s^{-1} , pH: 2, recovery: 1%).

As shown in Figure 5.4, the pure water permeability decreases in the order $\text{NF99HF} \geq \text{NP010} > \text{UTC-60} > \text{NF345HP} \geq \text{NE-70} > \text{NF-90} \geq \text{NF} > \text{RO90}$. A correlation between this order and the MWCO of the membranes fits if NP010 is disregarded. NF99HF has a 5 times smaller cut-off than NP010 but the permeability stays within the same range. Thus, the degree of hydrophilicity of the membranes active layer exerts an additional factor on the determined order. Meschke et al. (2018) measured the contact angle of NF99HF ($34.5 \pm 4.2^\circ$) and UTC-60 ($49.5 \pm 4.9^\circ$) and indicated that the active layer of UTC-60 is less hydrophile and thus, the permeability decreased [24]. In consideration of the contact angle of NP010 ($55 \pm 2^\circ$ [62]), the active layer is more hydrophobic, which seems responsible for the comparatively low permeability. In comparison, the contact angle of tightest membrane RO90 is $104.6 \pm 4.2^\circ$ [37] and thus, the membrane the most hydrophobic one, which referred to the lowest permeability.

However, the permeability depends on the porosity of the membrane, which is expressed by size, number, geometry, connectivity, and distribution of the pores [63,64]. The pore size of NF99HF is reported with 0.43 nm [35] and of NP010 between 0.33–1.33 nm

[59,65] and a higher pure water permeability could be expected for NP010, which was observed from Restolho et al. (2009) and Carvalho et al. (2011) [36,65]. The wide pore size distribution [65] and thus, the inhomogeneity of NP010 seem also responsible for the determined effect. The smallest pore size has RO90 (0.34 nm [66]) and thus, the lowest permeability.

However, in comparison to pure water, the permeability is significantly diminished in the case of a filtered synthetic feed solution. Due to the increased ionic strength of the solution, the osmotic pressure across the membrane is enhanced, which causes a flux decline and thus, the permeability decreases. Furthermore, the diffusive and convective mass transfer are affected by concentration polarization layer on the feed side of the membrane and thus, the permeability of the solutes [67]. Concentration polarization is reduced by high flow velocities, a turbulent flow regime or less solutes in solution [68]. Thus, the influence of the mentioned process parameters was investigated.

5.3.2 Influence of process parameters and feed properties on the separation performance, flux, and permeability

In the following, the process parameters TMP, flow velocity, and recovery were altered to evaluate the influence on the retention, flux, and permeability. Moreover, the ionic strength as feed property was adjusted by varying the *Zn* concentration. This evaluation was performed with NF99HF due to the comparably high permeability and selectivity.

TMP and flow velocity

In the following, the influence of TMP (10–20 bar, interval: 5 bar) and flow velocity (*v*: 0.5–1.1 m s⁻¹, interval: 0.2 m s⁻¹) on the separation performance as well as on flux and permeability was evaluated for NF99HF (see Figure 5.5 and Figure 5.6).

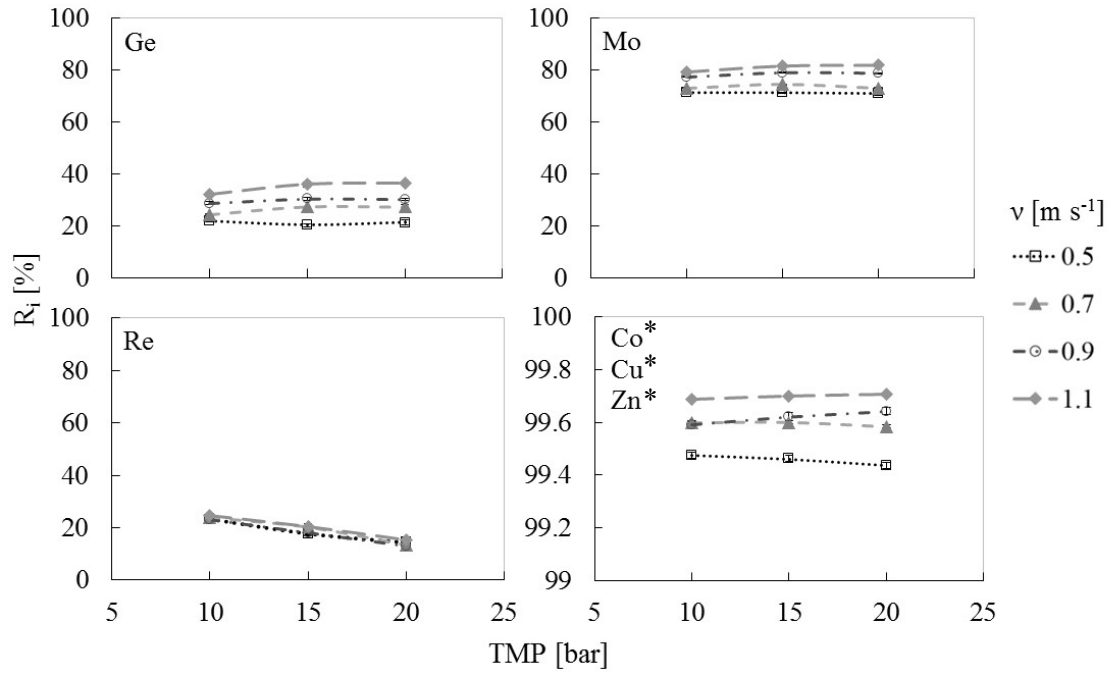


Figure 5.5. TMP-dependent *Ge*, *Mo*, *Re*, *Co*, *Cu*, and *Zn* retention R_i of NF99HF in dependence of flow velocity v for the synthetic feed with $3000 \text{ mg Zn L}^{-1}$ (T : 20°C , pH : 2, recovery: 1%) in comparison to deionized water (DW, v : 0.5 m s^{-1}). *shown is the averaged retention of the three elements.

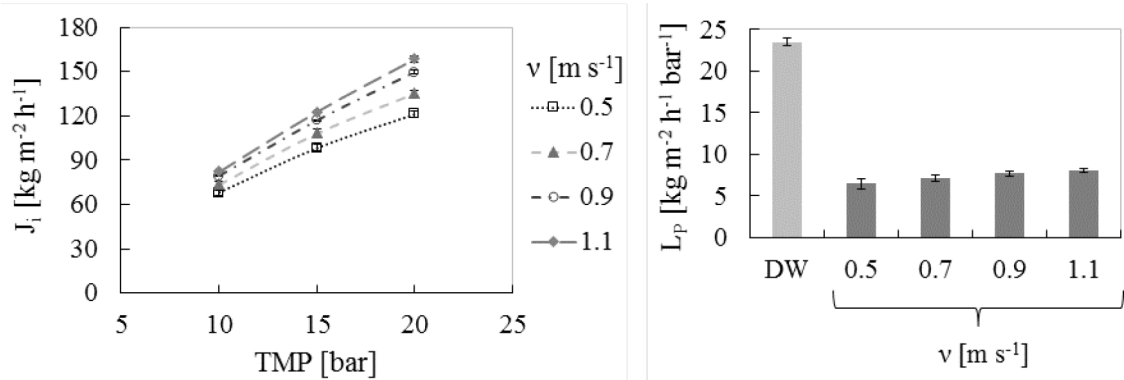


Figure 5.6. TMP-dependent flux J_i (left) and permeability L_p (right) of NF99HF in dependence of the flow velocity v for the synthetic feed with $3000 \text{ mg Zn L}^{-1}$ (T : 20°C , pH : 2, recovery: 1%) in comparison to deionized water (DW, T : 20°C , v : 0.5 m s^{-1}).

The influence of TMP is negligible for the uncharged solutes (*Ge*, *Mo*) and cations (*Co*, *Cu*, *Zn*) but for *Re*, the retention significantly decreases with increasing TMP (see Figure 5.5). It is supposed that the solvent and solute flux of *Re* increases due to transmembrane pressure enhancement. This effect seemed to dominate over the influence of flow regime. This phenomenon was observed in Meschke et al. (2018) for Cl^- ions too [24]. Konyuncu and Topacik (2003) reported this effect as well for low salt concentrations and low flow velocities [69].

As shown in Figure 5.5, with increasing flow velocity and thus with enhanced shear stress, retention increases. This can be observed for all elements but especially for the uncharged

solutes *Ge* and *Mo*. *Ge* retention achieved in average retentions between $21.2 \pm 0.8\%$ and $34.9 \pm 0.3\%$. For *Mo*, retentions between $71.3 \pm 0.3\%$ and $81.0 \pm 0.2\%$ were determined. The retention of uncharged solutes is mainly evoked by size exclusion. By the appearance of shearing forces, the convective transport orthogonal to the membrane is impeded and thus, the retention increased. The flow regime (laminar, transitional or turbulent) can be evaluated by the Reynolds number Re (see Eq. 4). Therefore, density ρ and dynamic viscosity η of the feed, flow velocity v , as well as the hydraulic diameter d_h (see Eq. 5) of the feed channel have to be considered.

$$Re = \frac{\rho \cdot v \cdot d_h}{\eta} \quad (4)$$

$$d_h = \frac{2 \cdot height \cdot width}{(height + width)} = 3.81 \text{ mm} \quad (5)$$

The calculated Reynolds number is approx. in the range between 1900 (laminar) and 4200 (turbulent). As shown in Figure 5.5, a laminar flow regime (0.5 m s^{-1}) is more appropriate for *Ge* separation because the convective transport into the permeate is less impeded.

For the negatively charged *Re* an influence of the flow regime on the separation performance was not observed. An increased shear stress should decrease the electric double layer over the membrane, which results in reduced concentration polarization and an enhanced permeation of charged solutes. Nevertheless, the *Re* retention is almost independent of flow velocity in the investigated range due to the fact that the impact of TMP is dominant.

For the cations, retention is nearly unaltered and $\geq 99\%$. The flow velocity and TMP have no influence on the steric hindrance of these ions, which is mainly responsible for the high retention. Nevertheless, flux and permeability are enhanced in case of an increased flow velocity (see Figure 5.6). Moreover, a linear flux increase in dependence of TMP can be observed. With increasing shear stress, the polarization layer is reduced and thus, osmotic pressure decreases and flux and permeability increases [68]. Due to the high ionic strength of the solution, lower pressures have not been tested because the applied driving force would be too low for a representative *Re* separation (see Figure 5.5) and flux decreases significantly (see Figure 5.6).

Ionic strength

The high ionic strength of the feed solution is evoked by the main component *Zn*, which is present as divalent cation. Furthermore, the high concentration of sulfate (SO_4^{2-}) and

hydrogen sulfate (HSO_4^-) has to be considered. It is assumed that SO_4^{2-} shields the charged membrane surface and HSO_4^- represents a permeation competitor [24]. Thus, the presence of these ions mainly influences retention of the other elements but especially of ReO_4^- as shown in Figure 5.7. Moreover, flux and thus, permeability is significantly affected by the high ionic strength of the solution (see Figure 5.8). To evaluate the influence of Zn on separation performance, the Zn concentration was altered.

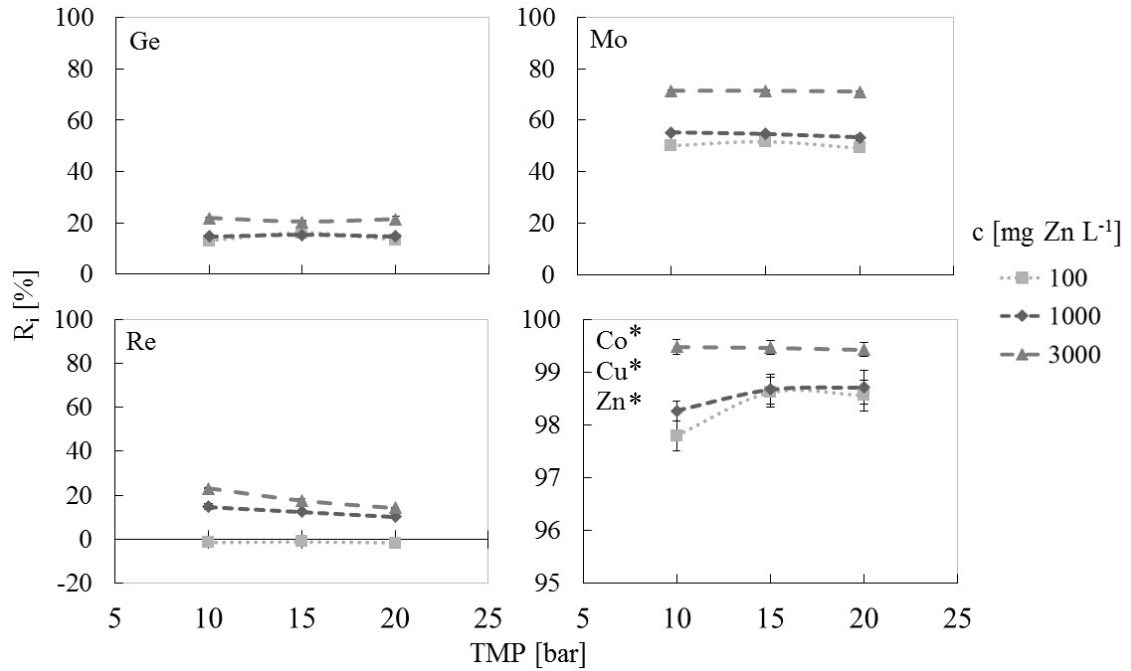


Figure 5.7. TMP-dependent Ge , Mo , Re , Co , Cu , and Zn retention R_i of NF99HF in dependence of Zn concentration for the synthetic feed (T : 20°C , v : 0.5 m s^{-1} , pH : 2, recovery: 1%). *shown is the averaged retention of the three elements.

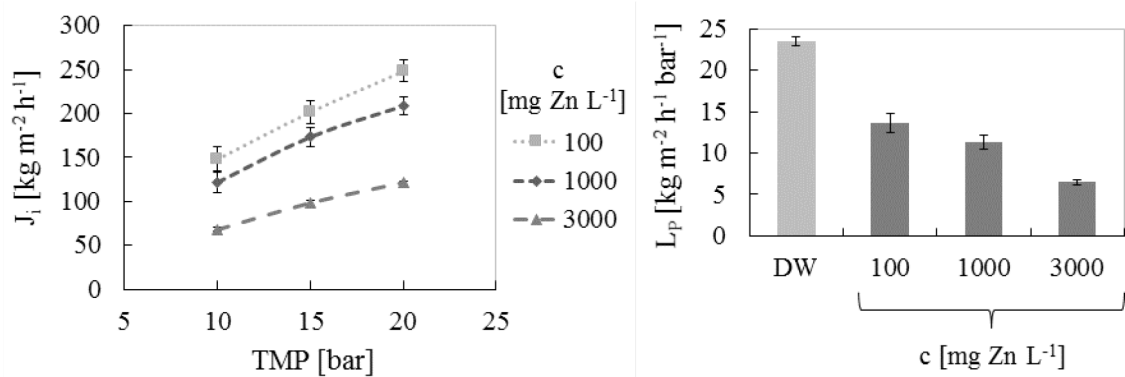


Figure 5.8. TMP-dependent flux J_i (left) and permeability L_p (right) of NF99HF in dependence of the Zn concentration for the synthetic feed (T : 20°C , v : 0.5 m s^{-1} , pH : 2, recovery: 1%) in comparison to deionized water (DW) (T : 20°C , v : 0.5 m s^{-1}).

As shown in Figure 5.7, a significant impact of Zn concentration on retention is determined for Re . Re retention is slightly negative for the lowest Zn concentration (100 mg L^{-1}) but with increasing Zn concentration (1000 and 3000 mg L^{-1}), Re retention is strongly

enhanced. Due to the enhanced presence of Zn^{2+} , the perrhenate is required for charge balancing as well, and thus, retention increases. Furthermore, concentration polarization increases with enhancing Zn concentration and less Re permeates.

Moreover, the Re retention decreases with increasing TMP, which was also determined in Meschke et al. (2018) [24]. Due to enhancing TMP, the turbulences above the membrane surface are increased, the polarization layer is reduced and thus, more Re permeates.

Zn concentration has nearly no influence on cation retention and only a marginal influence on Ge retention. For Mo , a slight retention increase is observed for the 3000 mg $Zn L^{-1}$ concentration. It can be assumed that the ionic species of Mo is more influenced by the presence of Zn than for Ge and thus, the retention of Mo increases with enhancing Zn concentration because a species change occurs.

As shown in Figure 5.8, flux is strongly affected by the Zn concentration of the feed. Due to the increasing osmotic pressure and enhancing polarization with increasing ionic strength of the solution, flux is decreasing and thus, the permeability (3000 mg $Zn L^{-1}$) is decreased by factor 3.6 compared to deionized water.

Recovery

A technical implementation of a NF membrane requires a high recovery in order to be economical and thus, recoveries between 10 and 80% were investigated for NF99HF (see Figure 5.9) due to its high permeability and good selectivity towards Re , Ge , and Mo in the conducted experiments. Moreover, NE-90 (see Figure 5.10) was utilized which showed a good separation performance towards Re and a comparatively high permeability.

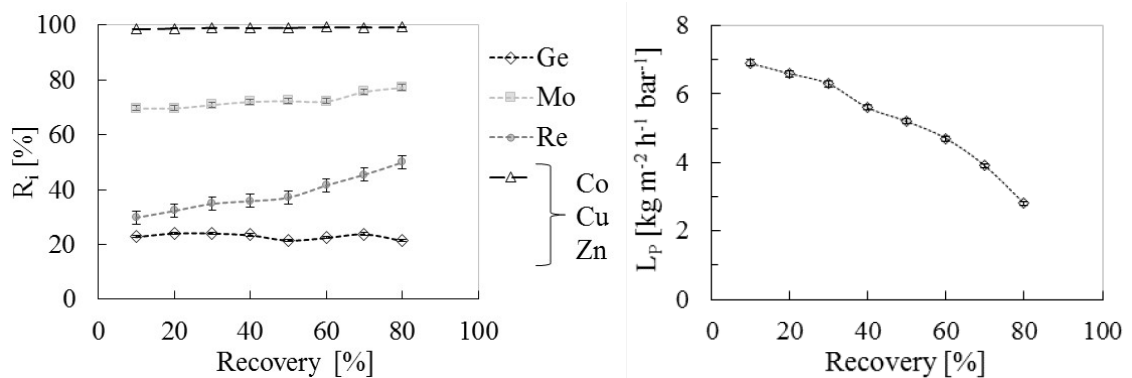


Figure 5.9. Retention R_i (left) and permeability L_p (right) of NF99HF in dependence of recovery for the synthetic feed with 3000 mg $Zn L^{-1}$ (TMP: 15 bar, T : 20°C, v : 0.5 $m s^{-1}$, pH: 2).

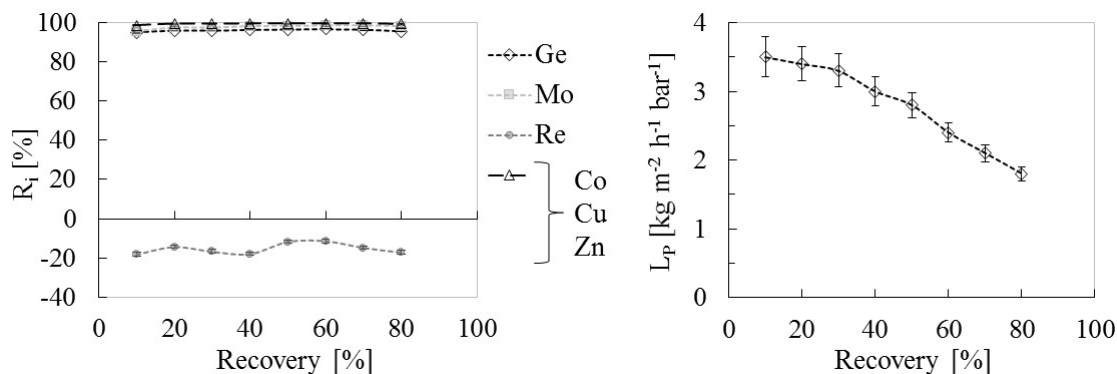


Figure 5.10. Retention R_i (left) and permeability L_p (right) of NE-90 in dependence of recovery for the synthetic feed with 3000 mg Zn L⁻¹ (TMP: 15 bar, T : 20°C, v : 0.5 m s⁻¹, pH: 2).

As shown in Figure 5.9, for NF99HF cation retention (Co , Cu , Zn) is $\geq 99\%$ and independent from recovery. Ge retention is almost constant ($23 \pm 2\%$) and independent from recovery too. Similar to the experiments with varying Zn concentration, Mo retention shows a slight retention increase in dependence of recovery ($66 \pm 1\%$ at 10% recovery, $77.5 \pm 0.5\%$ at 80% recovery). The same applies for Re , which shows a clear recovery dependency mainly evoked by the high Zn concentration, which increases in the retentate with enhancing recovery. This effect was also determined in experiments with altered Zn concentration (see Figure 5.7). However, permeability is constantly decreasing as recovery is enhanced due to the fact that the ionic strength of the retentate and thus, the osmotic pressure and the concentration polarization are increasing.

With NE-90, a Re separation is feasible (see Figure 5.10). Re retention is almost constant (approx. -15%) and independent of recovery. The same applies for uncharged solutes ($\geq 96\%$) and cations ($\geq 99\%$). Similar to NF99HF, permeability is decreasing if the recovery is enhancing. Compared to NF99HF, the permeability is only half as high (1.8 ± 0.1 kg m⁻² h⁻¹ bar⁻¹) but still moderate by achieving a recovery of 80%. However, NF99HF and NE-90 seems appropriate for the envisioned separation task and further investigations are aimed at reproducing the results with real bioleaching solution also in a spirally wound module.

5.4 Conclusion

The present study shows that a partial separation of strategic elements from a multicomponent leaching solution, which are present as mono and bivalent ions as well as uncharged solutes is feasible. In particular, Re (ReO_4^-) is separated by the membranes NE-90 and RO90. A separation of the uncharged components Ge ($Ge(OH)_4^0$) and Mo

($H_2MoO_4^0$) is, in general, possible. Here, NF99HF provides the best results (separation efficiency $\leq 50\%$) but the ionic radii of these elements are too close to each other and therefore, a complete separation not feasible with the tested NF membranes. The cation (Co^{2+} , Cu^{2+} , Zn^{2+}) retention is $>97\%$ for all tested membranes, except NP010 which is not suitable for the envisioned separation task. Nevertheless, the high ionic strength of the feed solution, evoked by the high *Zn* as well as sulfur concentration, decreases the permeability significantly and the separation performance of *Re* is affected negatively. With increasing *Zn* concentration or, in turn, with increasing recovery, *Re* retention is enhanced and thus, separation diminishes. It remains to be evaluated if a previous process step including *Zn* complexation or flocculation is appropriate to reduce the ionic strength of the leaching solution. Furthermore, it was observed that a higher TMP encourages the *Re* separation because the polarization layer is reduced. The influence of flow velocity on *Re* separation performance is negligible in the investigated range. Further investigations are focused on experiments with real leaching solution to reproduce the current data: moreover, the experimental data shall be accompanied by a mathematical model.

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6. Potential Process Chain

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Membrane Treatment of Leached Mining Waste – A Potential Process Chain for the Separation of the Strategic Elements Germanium and Rhenium

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Abstract

Microfiltration, nanofiltration, and reverse osmosis allow for separating multicomponent solutions. These membrane techniques are applied for the separation and concentration of several components on a scale of a micron down to an atomic range from aqueous solutions. This work showcases a potential process chain for the recovery of germanium and rhenium from an acidic bioleaching solution containing sludge particles. The focused feedstock is an anthropogenic mining waste (Theisen sludge) containing various valuable metals which were mobilized by bioleaching. For particle removal a rotating microfiltration (0.2 and 2.0 μm) system was utilized, showing that >99% of the leached sludge particles are retained. By nanofiltration >99% of the cationic transition metals were removed and the target elements germanium and rhenium are separated in reverse osmosis, which follows suit. Thereby, germanium remains in the retentate and rhenium is separated in the permeate. The filtered streams are intended for further downstream processes such as solvent extraction and adsorption.

6.1 Introduction

Globally, the increasing demand for valuable metals for high-tech applications continue to rise, resulting in increased dependencies on commodity markets [1–3]. In 2011, the European Commission defined a list of 14 critical raw materials (CRMs) for the European Union [2]. Subsequently, this list has been extended to 20 in 2014 [3] and to 27 CRMs in 2017 [1]. The majority of the CRMs are metals (e.g. *Ge*, *In*, *Sb*, *W*) [1], which occur naturally as mineral ores and are exploited by mining [4].

Bioleaching or bacterial leaching is an eco-friendly technology for metal mobilization from insoluble sulfide ores by biological oxidation [5,6]. The bacteria genus *Thiobacillus* is predominantly used in technically bioleaching processes in an acidic environment [5–8], at temperatures between 28–30°C [6]. Alternatively, an oxidative chemical leaching can be applied for primary sulfide minerals and secondary sulfidic matrices. Both versions enable in situ and ex situ leaching [9–12], allowing for the extraction of industrial metals such as *Al*, *As*, *Co*, *Cu*, *Ni*, *Zn*, and *U* from primary deposits or secondary, anthropogenic waste products [5,6,8,13,14]. This work presents the case for a deposited flue dust (220000 t Theisen sludge) from German copper shale smelting [15–17] as a feedstock of interest. As Figure 6.1 illustrates, the sulfidic sludge, which contains more than 15 critical or potentially critical raw materials (e.g. *Al*, *Co*, *Ga*, *Ge*, *Mg*, *Re*, *Sb*) [18] shall be mobilized by bioleaching. The resulting pregnant leaching solution (PLS) is to undergo downstream processing such as membrane techniques, adsorption, and solvent extraction.

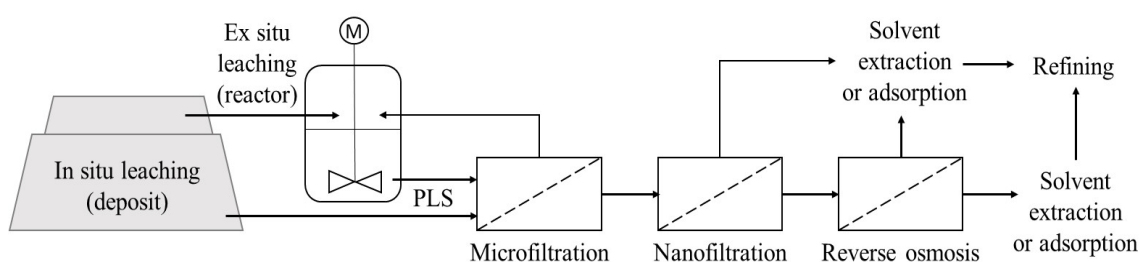


Figure 6.1. Potential process chain to mobilize and separate strategic elements from a mineral mining waste (Theisen sludge) by leaching (PLS – pregnant leaching solution) and downstream processes such as membrane treatment.

Within the r⁴-joint project [19,20], this complex research task is tackled. After metal solubilization, an acidic multicomponent bioleaching solution containing valuables over a wide range of concentrations is generated. This challenges the following separation and concentration process steps, as it renders the solution unsuited for traditional processing.

Here, different membrane techniques (micro- and nanofiltration, reverse osmosis) are applied to pretreatment, ion separation, and concentration. Membranes enable control over the rate of permeation and thus, permit separation of target components from a complex mixture at moderate process conditions [21].

Microfiltration (MF) membranes are already applied for purification and sterile filtration in biotechnology, food, pharmacology, and textile industry, to name a few [22,23]. In this context, they concentrate, purify or separate suspended particles, bacteria, colloids, and macromolecules $\geq 0.1 \mu\text{m}$ from solutions [24,25]. The separation is based on steric hindrance or sieving mechanisms [24]. Harnessing these qualities, MF is utilized for PLS pretreatment to remove Theisen sludge particles and bacteria. The MF membranes are manufactured from polymers or ceramics with a pore range between $0.1\text{--}10 \mu\text{m}$ [21,23–25]. Ceramic membranes are chemically and mechanically more resistant compared to polymeric membranes but manufacturing involves higher costs [23]. Transmembrane pressures between $0.1\text{--}2 \text{ bar}$ are applied and a permeability $>50 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}$ is achieved [24].

Nanofiltration (NF) membranes are currently utilized for water softening and -treatment as they reject molecules with a low molecular weight ($>200 \text{ Da}$), divalent ions ($R_i >90\%$) or to separate monovalent ions ($R_i <50\%$). NF membranes show characteristics of ultrafiltration (steric hindrance model) and reverse osmosis (solution-diffusion model) membranes [24,26]. The applied transmembrane pressure typically ranges from $5\text{--}25 \text{ bar}$ and permeabilities between $1.4\text{--}12 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}$ are commonly found [24]. Polymeric thin-film composite membranes are frequently employed [24,27] feature with a molecular weight cut-off (MWCO) between $250\text{--}2000 \text{ Da}$ [28]. This work targets the elements germanium (*Ge*) and rhenium (*Re*), separating them from an acidic multicomponent bioleaching solution using commercial NF membranes. By size exclusion, dielectric exclusion, solution diffusion, and adsorption mechanisms the separation is achieved [24,26].

In turn, commercial reverse osmosis (RO) membranes are utilized in the present study for concentration enhancement of separated elements to reduce the volume streams to be treated in subsequent processes such as solvent extraction. RO is state of the art with retentions $>98\%$ in an atomic and ionic range ($<200 \text{ Da}$) and currently applied for desalination, ultrapure water production or concentration (e.g. food and dairy industry). The transmembrane pressure reaches values between $10\text{--}100 \text{ bar}$ and permeabilities between $0.05\text{--}1.4 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}$ are common [24]. The transport is controlled by diffusion

and described by the solution-diffusion-model [28] for polymeric composite membranes [24,27,28].

In the present study, commercial ceramic and polymeric MF membranes (pore size: 0.2–2 µm) were utilized in a rotating cross-flow set-up to remove particles. The commercial thin-film composite membranes NF99HF and RO90 were tested for recovery and concentration of the target elements *Ge* and *Re* in cross-flow set-up. Currently literature data about the separation performance of membrane processes is sparse for both elements and is limited to own research and from the research group [18,29–32]. Thus, the developed process combines different membrane techniques (MF, NF, RO) and a separation of *Ge* and *Re* from the acidic and complex solution is achieved, which has not been demonstrated yet. This potential hybrid process is environmentally friendly and energy-efficient in addition to presenting a promising approach: combining remediation and strategic metal recovery enables simultaneous hazard removal and value creation.

6.2 Materials and Methods

6.2.1 Experimental Design

To separate the target strategic elements *Ge* and *Re* from the multicomponent bioleaching solution (section 6.2.2), various process steps are required. First, particles which remain from the leached Theisen sludge need to be removed. Therefore, a rotating microfiltration (MF_{CI}, section 6.2.3) system is envisioned. Our former study [34] shows that hydroxide particles are removed >99.9% without a significant loss of permeability. In the second process step remaining leaching bacteria shall be removed by microfiltration (MF_{CII}, section 6.2.3) and recycled for further leaching. Moreover, a polymeric MF membrane (MF_P, section 6.2.4) was tested for sterile filtration and compared to the ceramic ones. The pretreatment shall minimize fouling and ensure a high permeability in the conducted nanofiltration (NF, section 6.2.4). NF and reverse osmosis (RO, section 6.2.4) are required for ion separation and concentration of the target elements *Ge* and *Re*.

6.2.2 Bioleaching Solution

Within the r⁴-project [19,20] bioleaching was performed by the Interdisciplinary Ecological Center at the Institute of Biosciences, TU Bergakademie Freiberg [35]. The Theisen sludge was leached in 50 L barrels in a batch process at pH 2.3. These experiments were an upscaling from former bioreactor experiments [36,37]. By ICP-MS (Agilent Technologies Inc., 7700 Series), the concentration of trace elements was

measured. ICP-AES (Spectro Analytical Instruments GmbH, Ciros) was used for the main components as a consequence of the expected higher concentration. The composition of the PLS is shown in Table 6.1.

Table 6.1. Composition of the PLS (selected elements) after bioleaching of Theisen sludge in a 50 L barrel.

c_i [mg L ⁻¹]	Trace elements				Main components		
	<i>Co</i>	<i>Ge</i>	<i>Mo</i>	<i>Re</i>	<i>Cu</i>	<i>Fe</i>	<i>Zn</i>
PLS _I	0.38	0.25	0.10	0.16	54	1980	720
PLS _{II}	4.04	1.33	14.30	3.26			

I – original, II – enriched

Due to the fact that the extraction rate of bioleaching is further increased by process optimization [36,37], the concentration of the valuable trace elements was enriched (PLS_{II}) subsequently. Therefore, it was assumed that 100% of these elements can be extracted by bioleaching with a solid/liquid ratio 1:20.

6.2.3 Compact Rotating Disc Microfiltration Membranes – MF_{CI/II}

The first (MF_{CI}) and second (MF_{CII}) pretreatment of PLS were conducted with ceramic (α -Al₂O₃) compact rotating disc (CRD) membranes marketed by novoflow GmbH with a pore radius of 0.2 and 2.0 μ m. Here, Theisen sludge particles and leaching bacteria were removed to achieve a clear and sterile solution. On the basis of own studies [34], the ceramic membranes were chosen due to high particle retentions and mechanical, thermal and chemical resistance. The characteristics of the utilized membranes are shown in Table 6.2.

Table 6.2. Characteristics of the utilized ceramic compact rotating disc (CRD) membranes (0.2 and 2.0 μ m). Information was provided by the manufacturer.

Characteristic	CRD _{I/II}
r_o [mm]	76
r_i [mm]	12.5
s [mm]	4.5
A [m ²]	0.033*
pH range [–]	0–14
T_{max} [°C]	121

* Σ bottom and top side

Experimental Set-up

The ceramic membrane discs ($A_{max} \approx 0.1 \text{ m}^2$, see Table 6.2) were installed into the membrane module (see Figure 6.2) of the laboratory device CRD-01 manufactured by the novoflow GmbH with a storage capacity of 1.5 L and set into rotation. The number of revolutions was consistently at 1450 rpm [34]. The transmembrane pressure (TMP) was built up by a two-staged piston diaphragm pump (see Figure 6.3) and permeate pressed into the collecting channel. The TMP was monitored inside the CRD-01 by an electronically relative pressure sensor. Table 6.3 shows the applied TMPs during the experiments. Through the hollow shaft, permeate was led out pressureless and weighted on a precision scale (Kern & Sohn GmbH, Typ PCB 2500, readout: 0.01 g). Every 10 min a backwash period was applied with a backwashing pressure 1 bar above TMP to reduce fouling. Therefore, the permeate flow was reversed for 7 s. Furthermore, the turbidity was measured to evaluate the retention of CRD regarding the Theisen sludge particles.

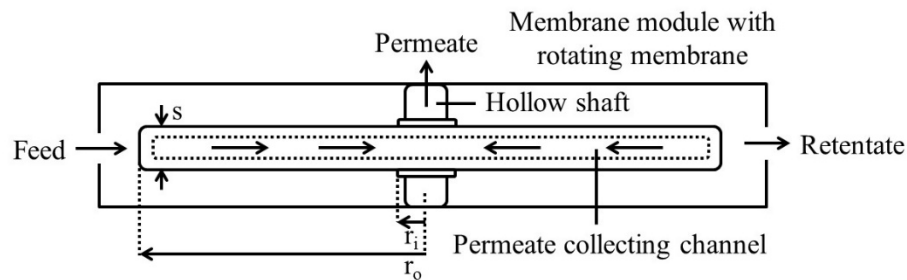


Figure 6.2. Schematic presentation of the compact rotating disc membrane module CRD-01 from the novoflow GmbH after [38], s – thickness, r_i – inner radius, r_o – outer radius.

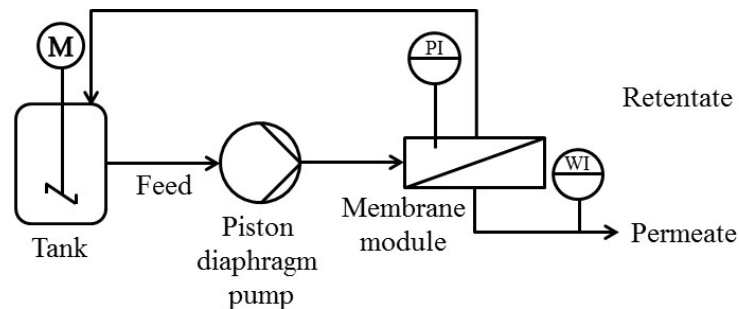


Figure 6.3. Schematic presentation of the compact rotating disc (CRD) microfiltration cross-flow set-up.

Table 6.3. Experimental design of the compact rotating disc (CRD) microfiltration set-up (TMP: 1.0 bar, T: 20°C, pH: 2.5).

Process step	Nominal pore size [μm]	Number of membranes	TMP [bar]	Recovery [%]
MF _{C1}	2.0	3	1.0	10–80
MF _{CII}	0.2	2	1.0	10–80

6.2.4 Polymeric Microfiltration (MF_P), Nanofiltration (NF) and Reverse Osmosis (RO) Membranes

In addition to ceramic MF membranes a commercial polymeric membrane (MV020, see Table 6.4) was tested for particle and bacteria removal as pretreatment (MF_P), which shall reduce fouling in the following NF process. MV020 is an often utilized polymeric MF membrane for clarification [39–41] and showed good results regarding particle removal in preceding own experiments. The separation performance of NF and RO towards the strategic elements was investigated with two commercial thin film composite membranes (NF99HF and RO90, see Table 6.4), which were chosen on the basis of our former studies [18,30], due to high selectivity, chemical resistance, and pure water permeability. Ceramic NF and RO membranes were not utilized due to the fact that the isoelectric point is typically between pH 6–8 [42,43] and thus, relocated compared to polymeric membranes (see Table 6.4). This refers to an enhanced anion repulsion under acidic conditions [43], which is counterproductive for the selective separation of *Re* [30].

Table 6.4. Characteristics of the utilized polymeric membranes. Unmarked information was provided by the manufacturer.

Characteristic	Membrane treatment		
	MF _P	NF	RO
	MV020	NF99HF	RO90 (NF97)
Manufacturer	Microdyn-Nadir Co. Ltd	Alfa Laval AB	Alfa Laval AB
Active layer	Polyvinylidene fluoride	Polyamide	Polyamide
$MWCO$ [Da]	0.2 μm^*	≥ 200	200
T_{max} [°C]	n. a.	50	50
p_{max} [bar]	n. a.	55	55
pH range [–]	1–12	3–10	3–10
IEP [pH]	–	4.1–4.4 ^{a)}	4.1 ^{c)}
R_i [%]			
$NaCl$	–	72 ^{b)}	≥ 90
$MgSO_4$	–	≥ 98	≥ 97
$L_p^\diamond$ [kg m ⁻² h ⁻¹ bar]	≥ 700	9–18 ^{b)}	1–6 ^{c)}

*nominal pore size

$^\diamond$ pure water

n. a. – not available

^{a)}[44], ^{b)}[45], ^{c)}[46]

Experimental Set-up

The cross-flow set-up for MF_P, NF, and RO is shown in Figure 6.4 and includes two membrane modules ($A_{each} = 76 \text{ cm}^2$), which are connected parallelly for double determination. The membranes are installed on a sinter discs due to mechanical resistance. The feed was transferred by a piston diaphragm pump (Verder Deutschland GmbH & Co. KG, Typ G03) and the TMP was built up by a pressure reducer valve (Badger Meter Europa GmbH, Typ RC 200). TMP and temperature ($T = 20^\circ\text{C}$) were kept constant during the experiments. Flow velocity was adjusted by the pump's flow rate and controlled by a flow meter (Meister Strömungstechnik GmbH, Typ DHGA-10). After all process parameters (TMP , T , v) stabilized (approx. 30 min), the experiment was started. The detailed experimental set-up is shown in Table 6.5. Permeate was led out pressureless and weighted on a precision scale (Kern & Sohn GmbH, Typ PCB 2500, readout: 0.01 g).

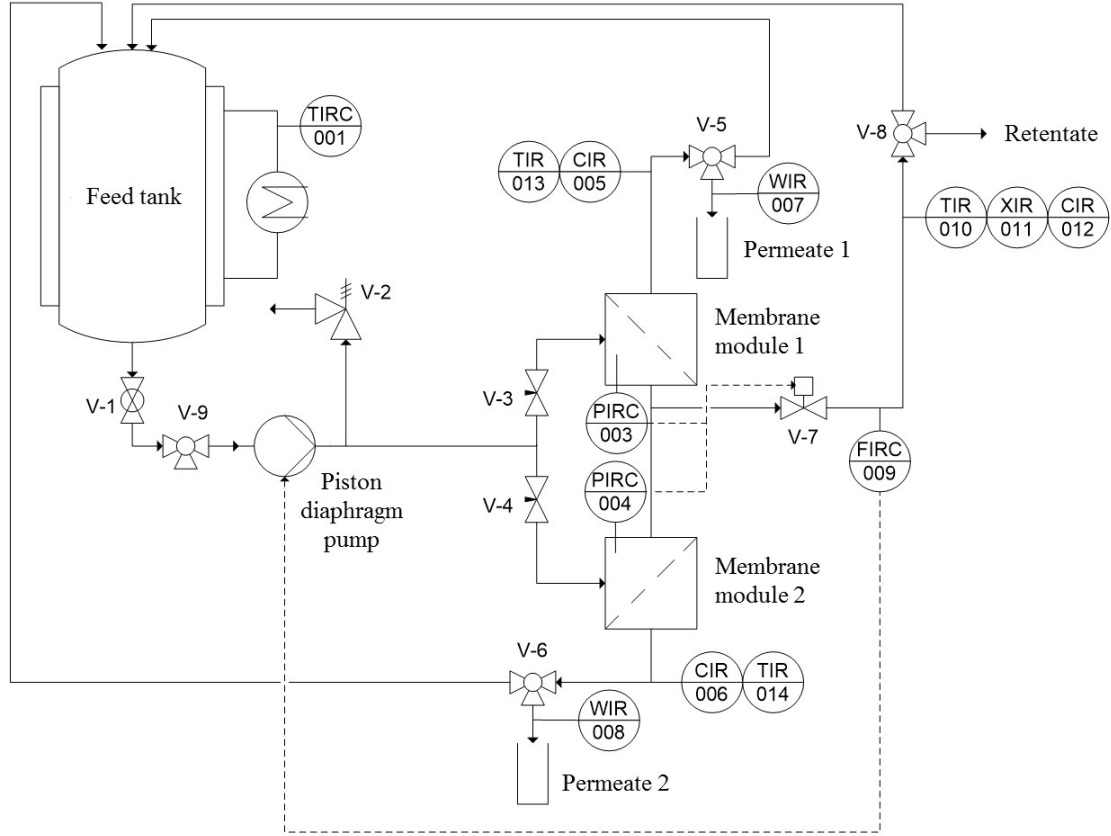


Figure 6.4. Schematic presentation of the polymeric microfiltration, nanofiltration, and reverse osmosis cross-flow set-up (W – mass, X – pH).

Table 6.5. Experimental design of the polymeric microfiltration, nanofiltration, and reverse osmosis cross-flow set-up (T : 20°C, pH: 2.5).

Process step	Membrane	MWCO [Da]	TMP [bar]	v [m s ⁻¹]	Recovery [%]
MF _P	MV020	0.2 μm*	1.0	0.7	≤80
NF	NF99HF	≥200 Da	15	0.5	≤80
RO	RO90	≤200 Da	15	0.5	≤80

*nominal pore size

6.2.5 Membrane Characteristics

During the experiments, recovery (see Eq. 1) was altered, which is the percentage ratio between the permeate mass m_p at the end of the experiment compared to the feed mass m_F at the beginning of the experiment.

$$\text{Recovery [\%]} = \frac{m_{p,t=\text{end}}}{m_{F,t=0}} \cdot 100\% \quad (1)$$

The retention R_i can be expressed by the ratio of the concentration of an ion c_i in the permeate to those in the feed (see Eq. 2). For the evaluation of retention regarding the turbidity (FNU), Eq. 3 has been applied.

$$R_i [\%] = \left(1 - \frac{c_{i,P}}{c_{i,F}}\right) \cdot 100\% \quad (2)$$

$$R_i [\%] = \left(1 - \frac{FNU_P}{FNU_F}\right) \cdot 100\% \quad (3)$$

The flux J_i (see Eq. 4) is represented by the collected permeate mass m_P over time t by unit membrane area A .

$$J_i [kg\ m^{-2}\ h^{-1}] = \frac{m_P}{A \cdot t} \quad (4)$$

The permeability L_p of the tested membranes can be expressed by Eq. 5, while taking the applied transmembrane pressure TMP into consideration.

$$L_p [kg\ m^{-2}\ h^{-1}\ bar^{-1}] = \frac{m_P}{A \cdot t \cdot TMP} \quad (5)$$

6.3 Results and Discussion

6.3.1 MF Pretreatment (MF_{Cl/ClI}) with Ceramic CRD Membranes

The PLS contained Theisen sludge particles with a median diameter of 1.25 μm and a mean diameter d_{50} of 1.55 μm respectively [15]. These particles should be removed by a 2.0 μm ceramic rotating disc membrane. The utilized piston diaphragm pump induced a strong pulsation inside the CRD-01 module and thus, the TMP achieved 0.94 ± 0.36 bar on average. Nevertheless, the pulsation does not have an adverse effect on flux because literature show that the permeate flux can be enhanced by flow pulsation [47,48]. Pulsation induces a turbulent flow, which can lead to a flux increase of up to 60% compared to a steady flow [48] and thus, fouling is reduced. The achieved flux over the test duration is shown in Figure 6.5. Process data (TMP , m_P , t) were recorded every 3 ms and data smoothing over 5 s was performed afterwards.

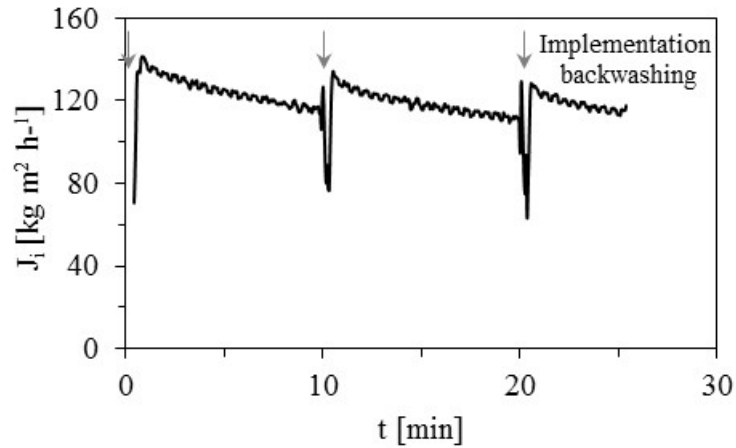


Figure 6.5. Flux J_i of the $2.0 \mu\text{m}$ CRD membrane over test duration for a target recovery of 10% with a backwashing period every 10 min (PLS_i , TMP: 1.0 bar, T : 20°C , N : 1450 rpm, backwashing pressure: 2.0 bar, backwashing duration: 7 s).

The flux is lowered at the beginning of the experiment and during the test duration as a consequence of the implementation of backwashing because the permeate volume flow is reversed. Backwashing was performed for all conducted experiments in the CRD-01 module with the same period (10 min) and duration (7 s), which is a recommendation of the manufacturer. By the backwashing conducted, the flux can be enhanced approx. 10–15% afterwards but the flux is steadily decreasing due to fouling. The temporary recovery of the original flux is a typical effect of backwashing. Nevertheless, the pores of the porous ceramic membrane are blocked by accumulating particles and fouling becomes more severe [49,50]. However, the achieved mean flux (10% recovery: $119 \pm 8.0 \text{ kg m}^{-2} \text{ h}^{-1}$) is comparable to our previous work [34] with a mine water sample, which contained precipitated iron hydroxide particles (1% recovery: $100 \pm 4.1 \text{ L m}^{-2} \text{ h}^{-1}$). Figure 6.6 shows the influence of the recovery (10–80%) on the flux.

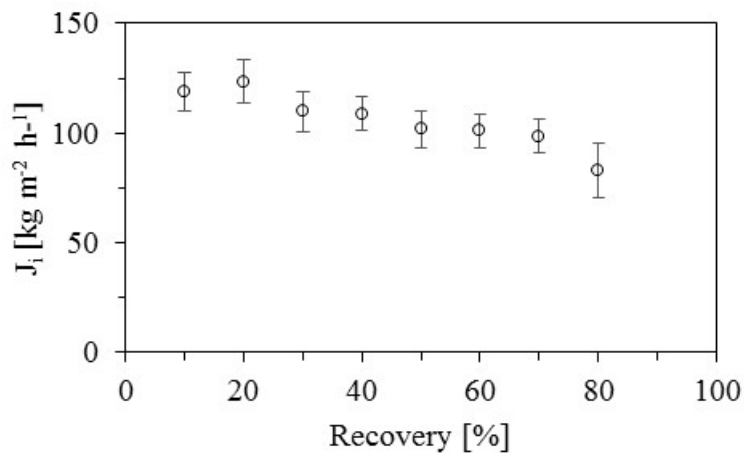


Figure 6.6. Flux J_i in dependence of the recovery for the $2.0 \mu\text{m}$ CRD membrane (PLS_i , TMP: 1.0 bar, T : 20°C , N : 1450 rpm, standard deviation $\leq 13 \text{ kg m}^{-2} \text{ h}^{-1}$).

The flux reaches mean values between $83\text{--}124\text{ kg m}^{-2}\text{ h}^{-1}$ and decreases with increasing recovery because pore blocking and fouling are enhanced. With increasing recovery, the backwashing effect is less effective due to the fact that pore blocking cannot be reversed. However, fouling could be reduced by enhancing the rotational speed or the implantation of turbulence promoters due to increased shear stress across the membrane surface. Moreover, a chemical cleaning could be applied to remove fouling layer and thus, for permeate flux recovery [49,51]. Previous work [34] shows that the positive effect of an ex situ cleaning (HNO_3 , pH 2, 60 min) is only temporary and fouling reappears quickly. Nevertheless, the flux still increases approx. 10% after backwashing even for a recovery of 80%. The achieved retentions in dependency of the recovery regarding the retained suspended Theisen sludge particles are shown in Figure 6.7.

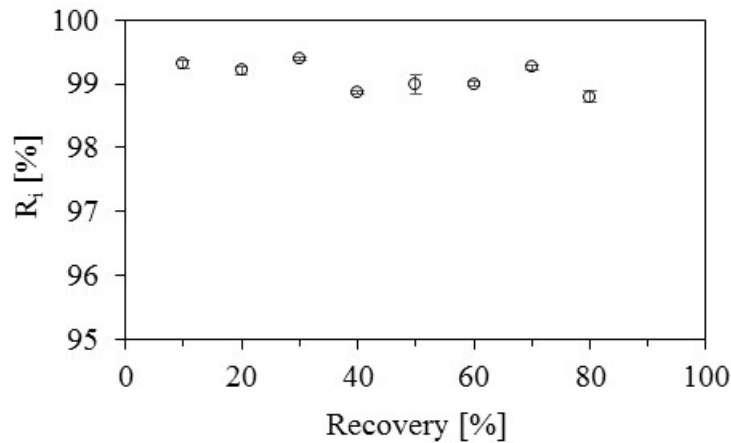


Figure 6.7. Retention R_i in dependence of the recovery for the $2.0\text{ }\mu\text{m}$ CRD membrane (PLS_I , TMP : 1.0 bar, T : 20°C , N : 1450 rpm, standard deviation ≤ 0.2).

The bioleaching solution had a turbidity of approx. 40 FNU and the $2.0\text{ }\mu\text{m}$ CRD membrane achieved retentions $\geq 99.1 \pm 0.1\%$ for all tested recoveries. Thus, the suspended Theisen sludge particles ($d_{50} = 1.55\text{ }\mu\text{m}$ [15]) are almost retained. Remaining particles and bacteria should be removed by the CRD membrane (second pretreatment – MF_{CII}) with a nominal pore size of $0.2\text{ }\mu\text{m}$ to get a sterile solution. However, the results of the $2.0\text{ }\mu\text{m}$ membrane indicate that a recovery of $\geq 80\%$ is adequate for particle removal as first pretreatment with a comparably high flux of $83 \pm 12\text{ kg m}^{-2}\text{ h}^{-1}$. The flux of the $0.2\text{ }\mu\text{m}$ ceramic membrane in dependence of the recovery is shown in Figure 6.8.

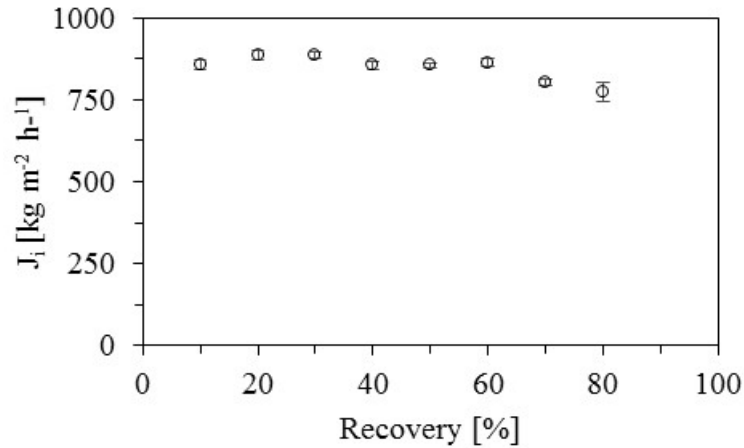


Figure 6.8. Flux J_i in dependence of the recovery for the 0.2 μm CRD membrane (PLSi, TMP: 1.0 bar, T : 20°C, N : 1450 rpm, standard deviation $\leq 30 \text{ kg m}^{-2} \text{ h}^{-1}$).

In comparison to the 2.0 μm CRD membrane, the flux of the 0.2 μm membrane is strongly improved and achieved mean values between 773–888 $\text{kg m}^{-2} \text{ h}^{-1}$. Ding et al. (2006) and Tu and Ding (2010) indicated comparable fluxes of approx. 450–550 $\text{L m}^{-2} \text{ h}^{-1}$ ($A_{\text{total}} = 0.121 \text{ m}^2$, TMP = 1.0 bar, $N = 1037\text{--}1930 \text{ rpm}$) for 0.2 μm ceramic disc membranes ($r_o = 45 \text{ mm}$) even for suspensions with a solid load of 100–200 $\text{g CaCO}_3 \text{ L}^{-1}$ ($d_{50} = 2.5 \mu\text{m}$) [52,53]. The reasons for this seem differences between the rotational speed N and outer radius r_o of the ceramic membrane disc, which have an influence on the peripheral velocity v_p (see Eq. 6).

$$v_p [\text{m s}^{-1}] = N \cdot \pi \cdot r_o \quad (6)$$

Due to the fact that the membranes utilized have a larger radius than prior literature [52,53], peripheral velocity (5.8 m s^{-1}) is increased and the flux enhanced. Bouzerar et al. (2000) investigated the influence of membrane radius and rotational speed on the flux and showed that flux is steadily increasing with increasing radius and rotational speed [54].

Nevertheless, the 0.2 μm membrane has an approx. 8-fold increased flux than the 2.0 μm ($106 \pm 13 \text{ kg m}^{-2} \text{ h}^{-1}$) membrane at a feed turbidity of $\leq 0.5 \text{ FNU}$. The main force responsible for this effect seems particle accumulation or biofouling, respectively, inside the pores of the 2.0 μm membrane, which may destroy the membrane's structural integrity [51]. The pure water flux of the 2.0 μm membrane achieved values of $1670 \pm 31 \text{ kg m}^{-2} \text{ h}^{-1}$ at 1.2 bar [34] and shows the significant flux decline in comparison to the bioleaching solution. Therefore, the first pretreatment (2.0 μm) may be skipped because the 0.2 μm membrane removes particles $\geq 99.9\%$.

Retention regarding the leaching bacteria *Acidithiobacillus ferrooxidans* [36,37] was not tested because it has an average size between 0.2 and 1.6 μm [55]. Moreover, the bacterial

cells accumulate [55] and thus, the solution should be sterile after the treatment with the 0.2 μm membrane. Still, biofouling occurred and decreased membrane performance over time. Therefore, a periodic permeate backwashing and the application of turbulence promoters are recommended. For a technical implementation, a sedimentation tank is envisioned after the ex situ bioleaching. If necessary, coagulants and flocculants can be added to enhance particle settlement. The decanted flow could be filtered by the CRD membrane afterwards with a recovery $\geq 80\%$. However, the retentate flow could be recycled for bioleaching because leaching bacteria are still present.

6.3.2 MF Pretreatment (MF_P) with a Polymeric Membrane (MV020)

In addition to the MF ceramic CRD membranes, a polymeric filtration step was tested. Here, a 0.2 μm membrane (MV020) was utilized. The determined flux over recovery is shown in Figure 6.9. Process data (TMP , v , pH , m_P , t , $\dot{V}_F$) were recorded every 1 ms and data smoothing over 5 s was performed afterwards. During the experiment, the recovery was steadily increased.

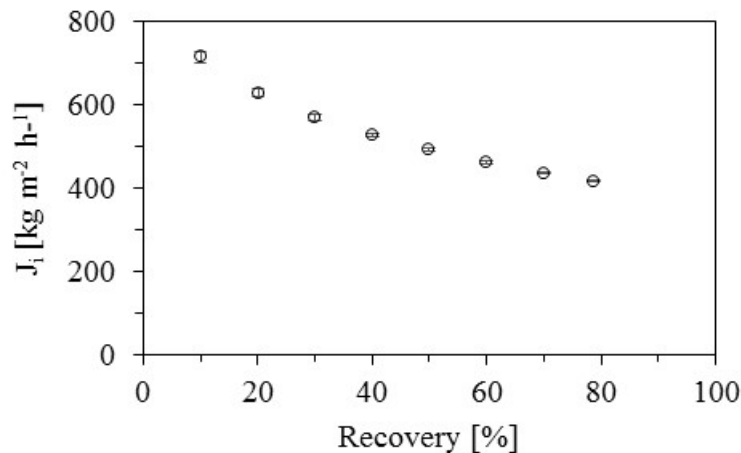


Figure 6.9. Flux J_i in dependence of recovery for MV020 (PLS_i , TMP : 1.0 bar, v : 0.7 m s^{-1} , standard deviation $\leq 13 \text{ kg m}^{-2} \text{h}^{-1}$).

Similar to the ceramic MF membranes, the flux decreased in dependence of recovery but more significant and achieved overall lower mean fluxes ($534 \pm 102 \text{ kg m}^{-2} \text{h}^{-1}$) compared to the 0.2 μm CRD membrane ($848 \pm 39 \text{ kg m}^{-2} \text{h}^{-1}$). The enhanced flux of the CRD membrane is a consequence of the increased flow velocity across the membrane surface due to rotation. Moreover, the ceramic membrane has a hydrophilic character and the polymeric is hydrophobic, resulting in enhanced flux of the ceramic ones. Summing up, MV020 shows slightly lower retentions ($\geq 98\%$) and thus, the rotating MF set-up seems

more adequate for the pretreatment of the PLS. The permeate flow was enriched in the following with the elements *Co*, *Ge*, *Mo*, and *Re* and transferred into NF set-up.

6.3.3 Separation and Concentration with Polymeric Nanofiltration (NF99HF) and Reverse Osmosis (RO90) Membranes

The pretreated and enriched bioleaching solution (PLS_{II}) was filtered in the next step with NF99HF for strategic element separation. In the acid bioleaching solution (pH 2), the elements are present as uncharged and charged ions, which has a significant influence on the retention. The received permeate (see Table 6.6) was treated with RO90 afterwards for further ion separation and concentration. Figure 6.10 shows the retention of both membranes in comparison to each other.

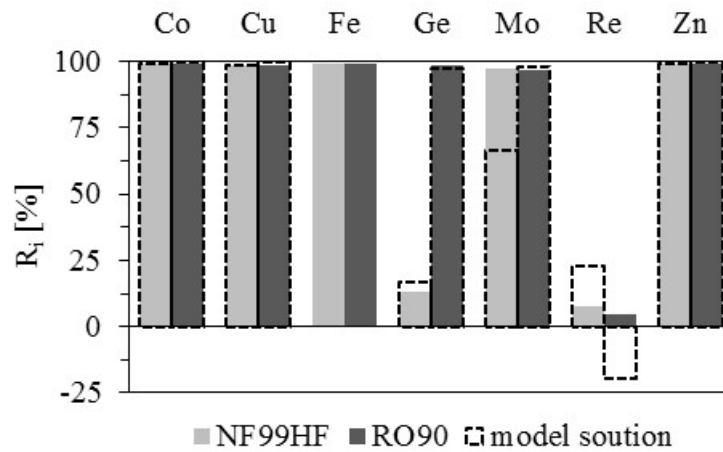


Figure 6.10. Retention R_i of NF99HF regarding the enriched pregnant leaching solution (PLS_{II}) and RO90 regarding the received permeate from NF99HF treatment (process parameters for both membranes: TMP: 15 bar, v : 0.5 m s^{-1} , recovery: 80%, standard deviation: NF99HF $\leq 0.8\%$, RO90 $\leq 0.7\%$) in comparison to the model solution (process parameters for both membranes: TMP: 15 bar, v : 0.5 m s^{-1} , recovery: 1%, standard deviation: NF99HF $\leq 1.1\%$, RO90 $\leq 0.5\%$ [30,33]).

Previously, own studies [18,29,30,33] investigated the separation behavior of NF99HF and RO90 intensively using a model solution. The retention of both membranes towards the model bioleaching solution [30,33] is also shown in Figure 6.10. The composition of the model solution, enriched pregnant leaching solution (PLS_{II}), and received permeate after NF99HF treatment is shown in Figure 6.6.

Table 6.6. Composition of the model solution [30,33] in comparison to the pregnant leaching solution (PLS).

c_i [mg L ⁻¹]	Trace elements				Main components		
	<i>Co</i>	<i>Ge</i>	<i>Mo</i>	<i>Re</i>	<i>Cu</i>	<i>Fe</i>	<i>Zn</i>
PLS _I	0.38	0.25	0.10	0.16	54	1980	720
PLS _{II}	4.04	1.33	14.30	3.26			
Permeate _{NF99HF}	0.04	1.18	0.39	2.96	0.74	15.0	7.8
Model solution	2.0	1.0	0.5	1.0	100	–	3000

I – original, II – enriched

Former experiments [30,33] with the model leaching solution were orientated to first leaching experiments with Theisen sludge [36]. The composition of the real leaching solution resulting from up scaled bioleaching experiments differs from these assumptions. Nevertheless, the trace element concentrations are in the same range and *Cu*, *Fe*, and *Zn* are the main components of the solutions.

As shown in Figure 6.10, the retention of the cationic transition metals (Co^{2+} , Cu^{2+} , Zn^{2+} , Fe^{3+}) is $\geq 99\%$ for both tested membranes and approx. 0.5% enhanced for RO90 due to the smaller MWCO. The retention of iron was not determined before [18,29,30,33] as the separation mechanisms of neutral, mono-, and divalent ions were the focus. However, the retention of the trivalent iron cation is enhanced by 0.3–0.5% compared to the divalent cations. Nevertheless, no significant influence on the retention as a consequence of the ion species (divalent or trivalent cation) was determined because the main separation mechanism is size exclusion. All cations exceed the effective pore radius or respectively the MWCO of the active layer of the membranes utilized.

For NF99HF, the *Mo* retention ($>97\%$) is increased compared to our former research [18,29,30,33]. In a comparable cross-flow set-up, the *Mo* retention achieved retentions $<70\%$ [30,33]. The main reason for this obvious difference is the enhanced *Mo* concentration due to the enrichment of the bioleaching solution in advance (see Table 6.6). As a consequence, the *Mo* species changed continuously from $H_2MoO_4^0$ (molybdic acid) to $Mo_8O_{26}^{4-}$ (octamolybdate) [56], which is excluded by size. Furthermore, the *Mo* anion formed is repulsed from the negatively charged membrane surface [30].

The retention of *Ge* ($Ge(OH)_4^0$) and, in particular, of *Re* (ReO_4^-) for NF99HF is decreased ($\leq 14\%$) in comparison to our former research [30]. By filtering the model bioleaching solution, the *Ge* and *Re* retention achieved 15–25% [30]. A change of the ion species can be ruled out because the present ion species are stable over a wide pH and concentration range [57,58]. It seems more likely that the presence of the trivalent *Fe* ion is responsible

for the decreased Re retentions. Fe^{3+} is retained $>99.2\%$ and thus, a small amount is transferred into the permeate. Therefore, anions (ReO_4^-) are required for charge balancing. In comparison to the experiments with the model solution, where only divalent cations were present [30], more Re is required to establish the Donnan equilibrium. For Ge , a co-permeation with Fe seems responsible for the decreased retention. Germanium shows a high affinity towards iron, which can be confirmed by literature [59] and own precipitation experiments using H_2SO_4 (pH 2), $NaOH$ (pH 10), and a model solution containing Ge and Fe (pH 2: $1000 \mu g Ge L^{-1}$ and $500 mg Fe L^{-1}$, pH 10: $2 \mu g Ge L^{-1}$ and $0.3 mg Fe L^{-1}$, $\geq 99\%$ co-precipitation).

With RO90 it is possible to separate Re but the retention has changed from -20% for the model solution to $>4\%$ with the real bioleaching solution. The composition of the filtered solution exerts a major influence here. In comparison to the model solution, the amount of cations in the feed (permeate from NF99HF) is strongly decreased and thus, the correlation between cations and anions more balanced. Therefore, less Re is required for charge balancing and retention improved. All other elements, especially Ge remain in the retentate (retention $\geq 97\%$). The determined concentration of the elements is shown in Figure 6.11 and Figure 6.12 for both permeate and retentate.

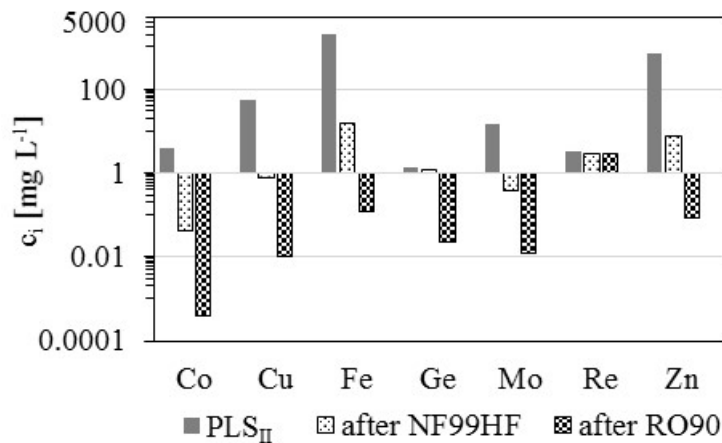


Figure 6.11. Element concentration c_i in the permeate after treatment with NF99HF and RO90 in comparison to the PLS_{II} (standard deviation: NF99HF $\leq 14\%$ for $\mu g L^{-1}$ (ICP-MS) and $\leq 2.3\%$ for $mg L^{-1}$ (ICP-AES), RO90 $\leq 16\%$ for $\mu g L^{-1}$ (ICP-MS) and $\leq 1.4\%$ for $mg L^{-1}$ (ICP-AES)).

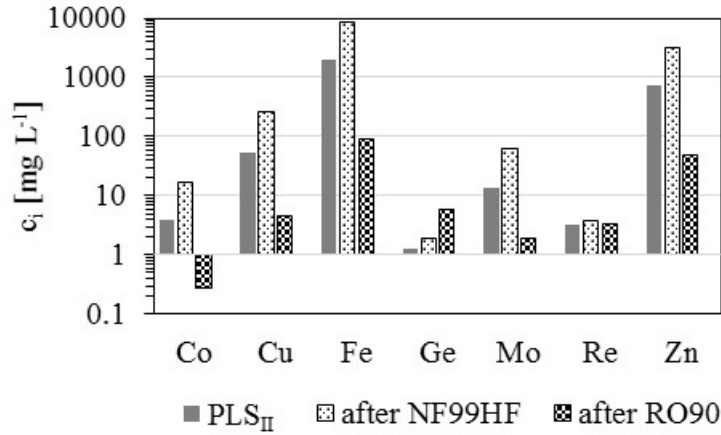


Figure 6.12. Element concentration c_i in the retentate after treatment with NF99HF and RO90 in comparison to the PLS_{II} (standard deviation: NF99HF $\leq 14\%$ for $\mu\text{g L}^{-1}$ (ICP-MS) and $\leq 2.3\%$ for mg L^{-1} (ICP-AES), RO90 $\leq 16\%$ for $\mu\text{g L}^{-1}$ (ICP-MS) and $\leq 1.4\%$ for mg L^{-1} (ICP-AES)).

Highlighted by Figure 6.11, the permeate concentration of the cationic transition metals is $\leq 15 \text{ mg L}^{-1}$ for NF99HF and $\leq 0.12 \text{ mg L}^{-1}$ for RO90. The *Re* concentration in the permeates is almost constant and achieved $2.8\text{--}3.0 \text{ mg L}^{-1}$ and thus, an enrichment during RO treatment was not feasible. In the retentate (see Figure 6.12) iron and zinc are most concentrated for both membranes and a refining of retentate after NF99HF treatment becomes worthwhile. However, the retentate concentration of the target elements *Ge* and *Re* is not negligible but a further separation becomes increasingly difficult due to the enhanced concentration of the cationic transition metals. Therefore, additional research is needed to address *Ge* and *Re* separation from such solutions. The achieved permeabilities during filtration with NF99HF and RO90 are shown in Figure 6.13.

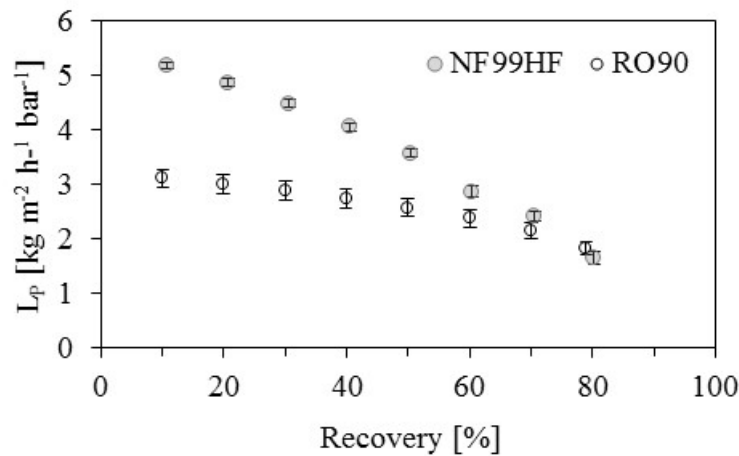


Figure 6.13. Permeability L_p of NF99HF and RO90 in dependence of recovery (TMP: 15 bar , v : 0.5 m s^{-1} , standard deviation: NF99HF $\leq 0.1 \text{ kg m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$, RO90 $\leq 0.2 \text{ kg m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$).

As shown in Figure 6.13, the permeability of NF99HF is enhanced by a factor of 1.7 compared to RO90 at a recovery $\leq 3\%$. With increasing recovery, both membranes are achieving nearly the same permeability ($\leq 2 \text{ kg m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$, $\geq 75\%$ recovery). Thereby, NF99HF shows a clear permeability decline of 70% (RO90 $< 40\%$). With enhanced recovery, the osmotic pressure is increasing and thus, the permeability is decreasing. Furthermore, the increasing concentration polarization affects the permeability negatively for NF99HF in particular. By increasing the shear stress across the membrane via turbulence promoters or enhanced flow velocity, the concentration polarization could be reduced but results in an increased Re retention and thus, a decreased separation selectivity [33].

Summing up, the utilized MF membranes allow for pretreatment of the PLS and removal of the remaining Theisen sludge particles from bioleaching. Nevertheless, a sedimentation might be appropriate prior to MF treatment. By NF, cationic transition metals (Co , Cu , Fe , Zn) and Mo were removed from the acidic multicomponent solution. In the RO conducted, it was possible to separate Ge and Re . A summary of the process steps and process conditions is shown in Figure 6.14. Moreover, the yield, which can be calculated according to Eq. 7 is presented.

$$Yield [\%] = \frac{c_P \cdot V_P}{c_F \cdot V_F} \cdot 100\% \quad (7)$$

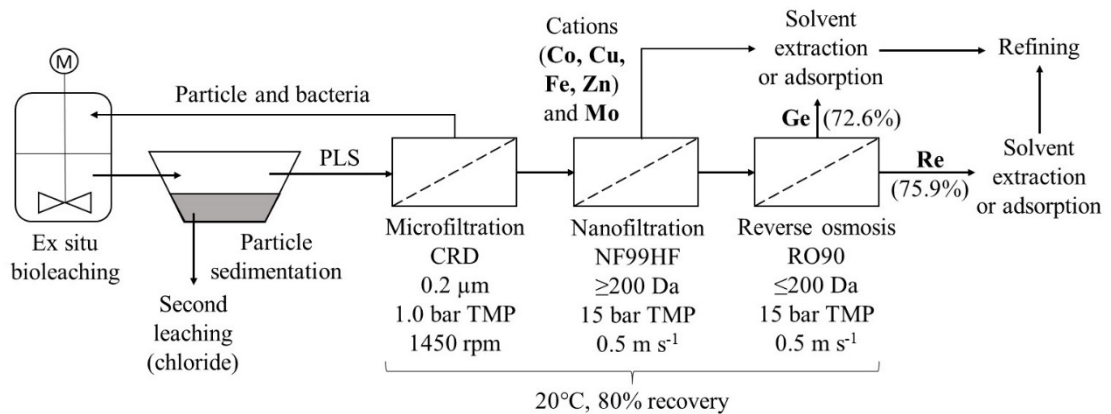


Figure 6.14. Potential process chain to mobilize and separate the strategic elements Ge and Re from Theisen sludge by bioleaching and membrane techniques (PLS – pregnant leaching solution, CRD – compact rotating disc). Process conditions and yields of membrane treatment are stated.

6.4 Conclusion

In the present study, a potential process chain for the separation of Ge and Re from an acidic multicomponent bioleaching solution was proposed and investigated by means of

MF, NF, and RO. For the MF pretreatment ceramic (CRD) and polymeric (MV020) membranes were tested for particle removal. The utilized rotating CRD membranes (0.2 and 2.0 μm) show retentions $\geq 99.9\%$ regarding the leached Theisen sludge particles but the 0.2 μm membrane showed an 8-fold increased flux. A particle ($d_{50} = 1.55 \mu\text{m}$) accumulation inside the pores of the 2.0 μm CRD membrane leads to intensified fouling and thus, flux decreased. In comparison, the mean flux of the 0.2 μm polymeric membrane MV020 was decreased approx. $300 \text{ kg m}^{-2} \text{ h}^{-1}$. The rotational speed has a positive effect on flux, due to the increased flow velocity across the membrane's surface. Moreover, the hydrophilic character of the ceramic membrane leads to a flux enhancement. Therefore, the 0.2 μm CRD membrane is recommended for pretreatment of the bioleaching solution. An additional suggestion is a sedimentation tank prior to the process chain. The retentate from MF can be recycled for bioleaching because leaching bacteria are still present. In the next step, the sterile solution is transferred into NF set-up. With NF99HF it is possible to remove all cations ($\geq 99\%$) and *Mo* ($>97\%$). The permeate stream is processed in the next step with RO90. Thereby, the strategic element *Ge* remains in the retentate and *Re* is separated into the permeate but a concentration of *Re* is not possible in parallel. Within the r^4 -joint project [19,20] it is envisioned to process the separated streams from NF and RO with solvent extraction and adsorption (ion exchange) [12,60,61]. However, the presented process chain represents a possibility for a membrane upscaling with spiral-wound modules. A comparable membrane pilot plant is currently in operation at the research and teaching mine "Reiche Zeiche", installed by the Institute of Thermal, Environmental and Natural Products Process Engineering at Freiberg University and aimed at investigating to separate *Ge* from a comparable complex bioleaching solution [62]. Future work is set to focus on mathematical transport modeling of nanofiltration to predict the separation behavior of multicomponent solutions.

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7. Discussion

In this chapter, the scientific results from the four peer-reviewed paper (chapter 3–6) are summarized and discussed. The aim is to evaluate the feasibility of membranes for the separation of the strategic elements *Ge* and *Re* from leaching solutions.

Table 7.1. Overview of conducted investigations (chapter 3–6).

Chapter	Membrane	Set-up	Process parameter	Element	Aim
3	NF99HF UTC-60 NP010	Dead-end	<i>TMP</i> : 15 bar <i>N</i> : 500 rpm <i>pH</i> : 2, 4, 7	<i>Ge</i> , <i>Mo</i> , <i>Re</i> , <i>Co</i> , <i>Cu</i> , <i>Zn</i>	Influence of pH on separation performance
4	NF99HF UTC-60	Cross-flow	<i>TMP</i> : 15 bar <i>v</i> : 0.5 m s ⁻¹ <i>pH</i> : 2	<i>Ge</i> , <i>Mo</i> , <i>Re</i> , <i>Co</i> , <i>Cu</i> , <i>Zn</i>	Influence of membrane characteristics on separation performance
5	NF99HF (NF, RO90, UTC-60, NE-70, NE-90, NF345HP, NP010)	Cross-flow	<i>TMP</i> : 10–20 bar <i>v</i> : 0.5–1.1 m s ⁻¹ <i>pH</i> : 2	<i>Ge</i> , <i>Mo</i> , <i>Re</i> , <i>Co</i> , <i>Cu</i> , <i>Zn</i>	Influence of process parameters on separation performance
6	MF: 0.2 and 2.0 μm CRD NF: NF99HF RO: RO90	Cross-flow Cross-flow	<i>TMP</i> : 1 bar <i>N</i> : 1450 rpm <i>pH</i> : 2 <i>TMP</i> : 15 bar <i>v</i> : 0.5 m s ⁻¹ <i>pH</i> : 2	<i>Ge</i> , <i>Mo</i> , <i>Re</i> , <i>Co</i> , <i>Cu</i> , <i>Zn</i> , <i>Fe</i>	Potential process chain for technical scale-up

First of all, the basic suitability of commercial polymeric nanofiltration membranes (NF99HF, UTC-60, NP010) for strategic element separation was examined in dead-end screening experiments in a batch cell (see chapter 3). The utilized membranes differ regarding MWCO (200–1000 Da) and polymer (polyamide, poly(piperazine)amide, polyethersulfone), which was utilized for active layer manufacturing. The experiments should provide information about the fundamental separation behavior of the target elements *Ge* and *Re* because up to this point, literature was barely or non-existent. Furthermore, the influence of *Mo*, cationic transition metals (*Co*, *Cu*, *Zn*), and pH (2, 4, and 7) on the retention was determined due to the fact that the ionic species and membrane charge is pH-dependent and thus, the separation performance might be affected.

Experiments were conducted with model solutions, containing elemental concentrations, which referred to the bioleached Theisen sludge solution.

Under consideration of the experimental results, the *Ge* retention is almost pH independent due to the fact that the ionic species is not changing within the tested pH range. *Ge* is present as uncharged solute (germanic acid: $Ge(OH)_4^0$ [14]), which is rejected little by size. Membrane swelling and germanium oxoanion forming ($\geq$ pH 7: $GeO(OH)_3^-$ [14]) seem responsible for slight retention fluctuations.

The monovalent *Re* anion (perrhenate: ReO_4^- [23]) is not rejected by size. Moreover, interactions with the charged membrane surface and thus, electromigration are promoters of permeation. Conspicuous are the low *Re* but also *Ge* retentions of NF99HF (active layer: polyamide) at pH 2. The membrane surface carries a positive surface charge below the IEP (pH 4.1–4.4 [61]) due to the protonation of the amino groups ($-NH_3^+$ [62]). Therefore, attraction of ReO_4^- is enhanced and retention decreased. Furthermore, membrane swelling seems less pronounced and permeation of uncharged $Ge(OH)_4^0$ seems favored. However, an inhomogeneity of the membranes cannot be ruled out, which can affect the separation performance. For each experiment, a new membrane was cut out from a large sample sheet to assure equal starting conditions.

In contrast to *Ge* and *Re*, a significant influence of pH was determined for *Mo* as the ionic species is strongly pH-dependent and changes from a neutral solute (pH 2) to a divalent anion (pH 7) [63]. Hence, retention increases due to steric hindrance and repulsion with the negatively charged membrane surface.

Under acidic conditions, the transition metals *Co*, *Cu*, and *Zn* are present as divalent cations (Co^{2+} , Cu^{2+} , Zn^{2+} [64–66]) and thus, retention should be high due to steric hindrance and repulsion with the positively charged membrane surface. This was observed for *Co*, which is only present in traces in the bioleaching solution. For *Zn* and *Cu*, which are main elements of the solution, retention was strongly decreased at pH 2. The main responsibility for this phenomenon is the built-up concentration and electric field gradient in dead-end set-up, which forces the permeation of divalent cations. Thus, steric hindrance does not affect the system as much anymore. With increasing pH ($\geq$ pH 6), the hydroxo species ($Me(OH)^+$) of the transition metals are formed [64–66] and retained by size and thus, retention is rapidly enhanced. In case of lowered recovery (from 50 to 10%) the forcing gradients decreased, retention was also enhanced at pH 2 as

sieving became more dominant as separation mechanism. If the set-up is switched to cross-flow, selectivity is strongly enhanced (see chapter 4).

Overall, the investigations in chapter 3 show that nanofiltration membranes with a MWCO of 200–300 Da (NF99HF, UTC-60) are suitable for separation as envisioned downstream processing. However, a pH adjustment (pH 7), as part of a technical implementation, is currently not recommended due to the costs incurred. Therefore, the separation performance under acidic conditions (pH 2) in cross-flow set-up was investigated further. Thereby, the experiments focused on the effect of membrane characteristics on separation performance (see chapter 4).

In addition to membrane charge, morphology, hydrophilicity, and roughness of the membrane's active layer also affects the separation performance. First, the cross section of the utilized commercial nanofiltration membranes (NF99HF, UTC-60) was determined with SEM and it was observed that the active layers have a thickness of 0.8–1.1 μm , which is equivalent to published values (1 μm) [40]. The transport of solutes through nanofiltration membranes is based on solution-diffusion, next to sieving. Therefore, the thickness as well as the polymer, from which the active layer is made, is essential for the separation performance. Taking the effective thickness over porosity into consideration (see chapter 4 – Table 4.7), the solute retention can be predicted [59]. For the uncharged solute *Ge* and *Mo*, the reflection coefficients for the NF99HF were estimated, which fit quite well with the experimental results. Thereby, the increase of retention almost correlates with the solute radius as predicted by a model [67]. The neutral *Ge* species is mostly transferred into the permeate and the neutral *Mo* into the retentate. Due to the fact that the separation of *Ge* and *Mo* is mainly based on sieving, the retention was controlled by varying the process parameters, which was observed in chapter 5.

Moreover, the influence of membrane charge on flux and retention was investigated (see chapter 4). In dependence of processed polymer and pH, different functional groups are located on the membrane's active layer. For this reason, the determined zeta potential and location of the IEP of the utilized membranes varied, which affects the intensity of the pH-dependent membrane charge. Hence, the repulsion or attraction of charged solutes is reduced or more pronounced. The zeta potential was determined with *NaCl*, *MgSO₄*, and a model solution, containing *Co*, *Cu*, *Ge*, *Mo*, *Re*, and *Zn* in combination. It was examined that the zeta potential is more pronounced above the isoelectric point with *NaCl* and decreased with *MgSO₄*. In the presence of the model solution, the zeta potential was not overly pronounced because the membrane surface charge is shielded by the high ionic

strength of the solution, mainly evoked by the presence of bivalent ions. Therefore, charge interactions above the IEP are less important. Below the IEP, the intensity of the zeta potential differed for the utilized membranes. It was observed that a higher positive zeta potential leads to an enhanced attraction of monovalent anions (Cl^- , HSO_4^-) and thus, to a decreased retention of them. The retentions were examined in cross-flow set-up with TMP's between 10–20 bar. The determined effect was also observed for *Re* (ReO_4^-) and it seems adequate to modify the membrane surface for intensifying the permeation of *Re* to realize an improved separation from the multicomponent solution. The transition metals showed constant high retentions for both membranes as predicted in dead-end set-up (see chapter 3) due to steric hindrance.

Furthermore, the membranes differed regarding roughness and hydrophilicity. The membrane (NF99HF), which was smoother and more hydrophilic (lower contact angle) showed a higher flux and should have a lower fouling tendency, which is highly significant in technical applications.

The influence of TMP, flow velocity, flow regime, and recovery on the separation performance was determined with NF99HF in cross-flow. This membrane showed the best results in screening experiments in dead-end (see chapter 3) and conducted cross-flow experiments (see chapter 4). The experimental results indicate that the permeation of the uncharged solutes increases with enhancing flow velocity. Moreover, a laminar flow regime seems more adequate for the separation process due to the fact that *Ge* and *Re* are mostly transferred into the permeate. An influence of TMP was only determined for *Re* and experiments show that retention decreases with increasing TMP. Moreover, an increase of recovery from 10 to 80% leads to an enhanced *Re* retention due to concentration polarization. The retention of uncharged *Ge* and *Mo* ions remains unaffected by TMP. However, the Donnan effect is essential for the separation behavior of *Re*. Since the aqueous solution is sulfate rich, the presence of HSO_4^- needs to be considered, which is a permeation competitor for *Re*.

In chapter 6, the generated data and information gained from chapter 3–5 were conglomerated to develop a process chain for a proposed scale-up to separate the targeted strategic elements *Ge* and *Re* from the multicomponent bioleaching solution. As the leaching solution contains particles and bacteria, a removal of them is essential as pretreatment to prevent fouling. Therefore, a rotating and conventional tangential cross-flow microfiltration (0.2 and 2.0 μm) was studied with polymeric and ceramic membranes. Investigations show an increased flux in the rotating set-up due to an

enhanced flow velocity and thus, increased shear stress across the membrane surface. In both set-ups, particle retention was comparable ($>99\%$).

The particle-free and sterile solution was treated with NF99HF to remove all cationic components $\geq 99\%$ (*Cu*, *Co*, *Fe*, *Zn*). *Mo* was also retained ($>97\%$), which can be separated from the cations by solvent extraction afterwards [39]. In the next step, *Ge* and *Re* are separated with RO90. Thereby, *Ge* almost exclusively remains in the retentate ($R_i \geq 97\%$) and *Re* is transferred into the permeate ($R_i < 5\%$). A concentration is not feasible in cross-flow, neither in dead-end set-up. The small hydrated radius and high diffusion coefficient of *Re* seems responsible for this effect, which enables a free permeation to establish equilibrium conditions. Furthermore, *Re* is required for charge balancing of the cationic components and thus, less transferred to the permeate. Therefore, a concentration by adsorption or solvent extraction is envisioned within the r⁴-joint project. The envisioned membrane processes are recommended for prefractionation within the hybrid downstream processing.

8. Conclusion and Outlook

The present cumulative work investigated the feasibility of membranes, in particular nanofiltration for the separation of the strategic elements *Ge* and *Re* from a complex leaching solution. Both elements have a high economic relevance as they are required for high-tech production. The mining residue studied (Theisen sludge) contains these elements in considerable amounts. Via bioleaching, the bonded metals can be mobilized into an acidic, sulfate-rich, multicomponent solution. The unique selling point of nanofiltration is the selectivity towards mono- and bivalent ions and thus, this kind of downstream processing seems suitable.

The fundamental pH-dependent separation performance of *Ge* and *Re* was investigated in dead-end screening experiments with three commercial nanofiltration membranes (NF99HF – Alfa Laval, UTC-60 – Toray, NP010 – Microdyn Nadir) using model solutions. The experimental results show, that pH as well as the MWCO and membrane charge have an influence on the retention. Moreover, investigations indicate that a separation of the neutral *Ge* species and monovalent *Re* anion from the complex leaching solution is feasible. However, dead-end is not recommended due to the built-up concentration and electric-field gradient, which have a negative effect on the separation selectivity and thus, cross-flow was focused in the following experiments.

In addition, the influence of membrane characteristics thickness, hydrophilicity, roughness, and zeta potential on separation performance were investigated. It was observed that a high ionic strength shields the membrane surface charge and thus, the electromigrative transport is diminished. Moreover, the flux was strongly decreased in comparison to pure water. The hydrophilicity and roughness showed little influence on separation performance. Thereby, it was observed that a smoother and more hydrophilic membrane (NF99HF) has a higher selectivity towards *Ge*: permeation is less disturbed (higher flux).

Furthermore, the influence of the process parameters (TMP, flow velocity, recovery) on separation performance was investigated. Experiments were mainly conducted with NF99HF because this membrane tends to be the best fitting for the giving separation task as demonstrated in dead-end and former cross-flow experiments. It was examined that the flow velocity mainly influences the retention of the uncharged solutes (flow velocity $\uparrow \rightarrow$ retention $\uparrow$) and TMP affects the *Re* retention ($TMP \uparrow \rightarrow$ retention $\downarrow$). Furthermore, a high ionic strength evoked by a high *Zn* concentration (main component of the leaching

solution) affects the *Re* retention ($c_{Zn} \uparrow \rightarrow \text{retention} \downarrow$). An influence on the recovery was mainly determined for uncharged solutes, for *Ge* (recovery $\uparrow \rightarrow \text{retention} \uparrow$) in particular as concentration polarization diminishes permeation. The retention of cations (*Co*, *Cu*, *Zn*) was almost not affected by varying process parameters.

With the data collected from all investigations, a potential process chain for the separation of *Ge* and *Re* was elaborated for a scale-up. This process includes micro-, nanofiltration, and reverse osmosis. By MF, particles are removed >99% from the leaching solution. To ensure a sterile solution, a 0.2 μm membrane is recommended. The pretreatment is necessary to prevent fouling in the following NF process. A rotating MF system was tested next to conventional cross-flow and is preferred due to a higher flux evoked by enhanced shear stress. In the conducted NF (NF99HF), it is possible to retain the cationic transition metals (*Cu*, *Co*, *Fe*, *Zn* $\geq 99\%$) and the uncharged *Mo* species (>97%). The target elements *Ge* and *Re* are transferred into the permeate and can be separated in the following RO set-up with the commercial membrane RO90 (Alfa Laval). Nevertheless, the recommended membrane techniques are part of a complex hybrid process involving solvent extraction and adsorption as well, which were all part of the r⁴-joint project ‘Theisenschlamm’.

In this work, membrane experiments conducted contribute to explain the separation behavior of *Co*, *Cu*, *Ge*, *Mo*, *Re*, *Zn* (*Fe*) with NF in an acidic, sulfate-rich, multicomponent solution and thus, a research gap was closed. Thereby, the influence of the solution (pH, ionic strength), membrane characteristics (thickness, hydrophilicity, roughness, zeta-potential), and process conditions (TMP, flow regime, flow velocity, recovery) were investigated and significant effects determined. Summing up, with the utilized membranes NF99HF and RO90 a separation of *Ge* and *Re* from the multicomponent solution can be achieved and thus, a downstream processing is feasible. Further investigations could focus on membrane surface modification to enhance electromigrative transport and thus, an increased *Re* separation might be realized. Moreover, the shares of convection, diffusion, and electromigration to the solute transport were quantified by a model. Furthermore, experiments with a spiral wound module in long term experiments are recommended prior to a technical implementation.

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Appendix

A-1 Species Distribution Diagrams

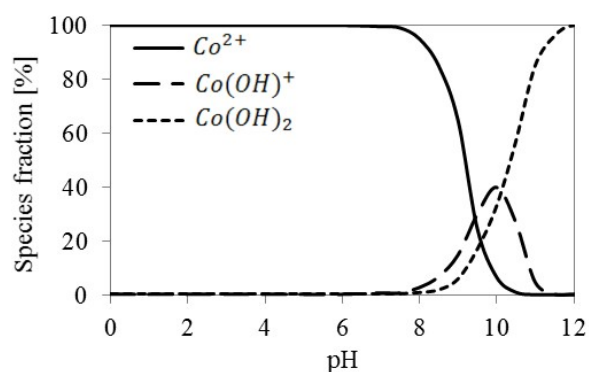


Figure A.1. Species Distribution diagram of Co(II) [A1]

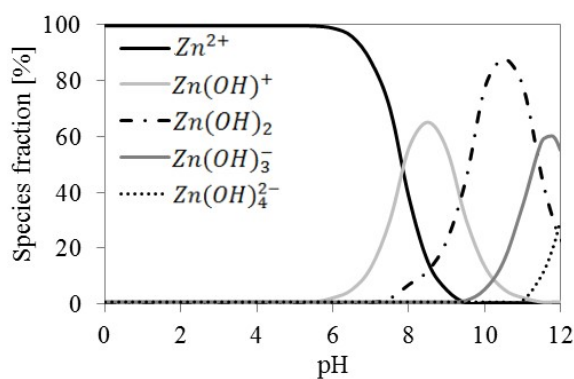


Figure A.2. Species Distribution diagram of Zn(II) [A2]

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A-2 Publications not included in this Work

A. Werner, K. Meschke, K. Bohlke, B. Daus, R. Haseneder, J.-U. Repke. Resource Recovery from Low-Grade Ore Deposits and Mining Residuals by Biohydrometallurgy and Membrane Technology. Potentials and Case Studies. *ChemBioEng Reviews* 5(1) (2018) 6–17.

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A. Werner, K. Meschke, K. Bohlke, B. Daus, R. Haseneder, J.-U. Repke. Biohydrometallurgie und Membrantechnik zur Wertstoffgewinnung aus Armerzlagerstätten und bergbaulichen Altablagerungen (Biohydrometallurgy and Membrane technology for Resource Recovery from Low-Grade Ores and Mining Residuals). *Chem. Ing. Tech.* 89(1–2) (2017) 40–52.

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K. Meschke, K. Gumnior, B. Daus, R. Haseneder, J.-U. Repke, Nanofiltration – a new separation pathway in secondary mining, In: C. Drebenstedt, M. Paul (Eds.), *Mining Meets Water: Conflicts and Solutions: Proceedings IMWA 2016*, Freiberg, Germany, 2016, pp. 1356–1363.

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A-3 Conference Contributions

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