



# 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.

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## 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. 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 (engl. Theisen sludge), represents the feedstock for a proposed hybrid process, which shall include bioleaching and downstream processes like nanofiltration.

### 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<sup>-1</sup> and was dewatered to about 60 g L<sup>-1</sup>. 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 220,000 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

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restored at a mono-landfill site called Teich 10 (engl. 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 1.

The metals lead and zinc are predominant in the Theisen sludge (see Table 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 ( $\beta$ -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.

## 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 days at 30 °C [16]. The performed bioleaching demonstrates that valuable strategic elements can be solubilized from Theisen sludge (see Table 2) but further process optimization is required to increase the extraction yield [16,26].

The mobilized elements need to be separated and concentrated from the complex multicomponent leaching solution with a wide range of concentration (see Table 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.

## 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.  $\text{Na}^+, \text{Cl}^-$  <50%) and multivalent (e.g.

**Table 1**  
Literature review of the composition of Theisen sludge in comparison to the detected element concentration in the sampled sludge.

Element	Concentration [ $\text{mg kg}^{-1}$ ]							Sampled sludge
	Literature review							
	1992 <sup>a</sup>	1994 <sup>b</sup>	†1996 <sup>c</sup>	1997 <sup>d</sup>	1998 <sup>e</sup>	2004 <sup>f</sup>	†2015 <sup>g</sup>	2016 <sup>h</sup>
Ag <sup>**</sup>	430		320	240	520	350	n. a.	430
Al <sup>**</sup>	n. a.		n. a.	4700	23,600	9400	14,100	11,000
As	6500		5800	7000	4100	6300	7600	9100
Cd	400		790	350	360	380	400	290
Co <sup>*</sup>	n. a.		n. a.	60	80	n. a.	n. a.	130
Cr <sup>**</sup>	n. a.		n. a.	190	890	110	n. a.	n. a.
Cu <sup>**</sup>	12,000		12,000	11,700	14,100	12,300	16,000	12,100
Fe <sup>**</sup>	n. a.		n. a.	13,600	30,900	15,200	17,000	15,000
Ga <sup>*</sup>	n. a.		n. a.	40	80	n. a.	n. a.	n. a.
Ge <sup>*</sup>	60		n. a.	20	30	n. a.	n. a.	20
Mg <sup>*</sup>	n. a.		n. a.	9800	2500	2500	2600	n. a.
Mn <sup>**</sup>	n. a.		n. a.	920	670	740	340	640
Mo <sup>**</sup>	700		420	290	600	480	520	350
Ni <sup>**</sup>	100		n. a.	110	510	490	80	n. a.
Pb	140,000		121,000	132,000	122,000	81,300	134,000	97,900
Re <sup>**</sup>	100		n. a.	60	60	n. a.	30	90
S	160,000		n. a.	83,100	113,000	151,000	155,000	121,600
Sb <sup>*</sup>	4500		3900	2600	1500	4900	3200	2100
Si	n. a.		n. a.	54,100	n. a.	100,000	75,000	n. a.
Sn <sup>**</sup>	12,000		14,000	12,100	17,200	n. a.	14,100	n. a.
Ti <sup>**</sup>	n. a.		n. a.	3200	5000	700	n. a.	n. a.
Tl <sup>**</sup>	230		310	270	320	n. a.	n. a.	n. a.
V <sup>**</sup>	n. a.		n. a.	320	n. a.	n. a.	n. a.	n. a.
Zn <sup>**</sup>	180,000		139,000	149,000	163,000	241,000	184,000	250,400
Zr	n. a.		n. a.	10	970	n. a.	n. a.	n. a.

<sup>\*</sup> Critical raw material [1].

<sup>\*\*</sup> Candidate for critical raw material [1].

† Literature data in %, n. a. – not available.

<sup>a</sup> Refs. [6–8,10].

<sup>b</sup> Refs. [6–8,10].

<sup>c</sup> Refs. [9,12].

<sup>d</sup> Ref. [6].

<sup>e</sup> Ref. [13].

<sup>f</sup> Ref. [14].

<sup>g</sup> Ref. [15].

<sup>h</sup> Ref. [16].

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