Master’s Thesis Engineering Technology

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Advanced leaching and recovery technology to recover metals from a mineral waste stream via MOF formation chemistry

Student: Sam Haenen

Master of Chemical Engineering Technology

INTRODUCTION

The metal recycling industry has gain a lot of interest due to **environmental awareness**. Additionally, metal recycling has often the potential to reduce energy consumption, the use of natural resources and the risks for the human health[1]. The development of new recycling technologies can possibly create new **business opportunities in the future**. It is clear that the recycling industry can form a healthy combination of the human aspect together with the economical aspect. **Metal leaching** allows to reduce the risks of residue streams and the recovery of valuable metals. However, metal leaching from mineral residues is often **not/poorly selective**, resulting in leachates which contain a range of metals [2].

In this study it is proposed to recover metals via an **advanced leaching pathway** with a novel lixiviant: **triethylamine**. Furthermore, It is hypothesized that this leaching step could be coupled with a novel metal recovery technique for **valuable metals** (Zn, Cu, Ni and Pb). The addition of 2-methylimidazole is expected to result in the **selective formation** of a **metallic organic framework** (MOF) precipitate as a valuable end-product. The obtained MOF materials could be used for several applications, resulting in an effective recycling way of valuable metals.

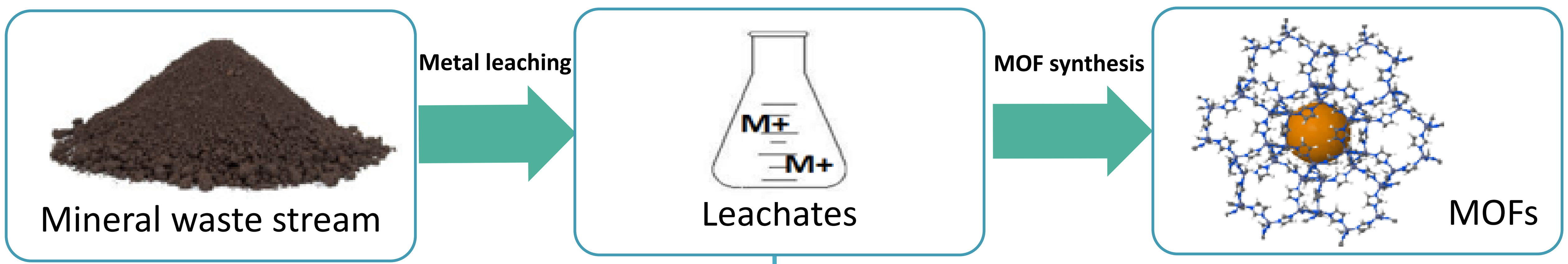

Figure 1. Schematic overview

METAL LEACHING

OBJECTIVES

- Determine **optimal leaching conditions** depending on the effect of triethylamine (TEA), reaction time

APPROACH

Scientific background

Selective way to **gain metals**, present in small amounts (<5%wt), with a **high efficiency** [3]

- Raw material is a **tailing**: waste stream originating from metal production of primary resources

Figure 2. Tailing pond

large recycle **opportunities**:

1. valuable metal fraction in ores is small => millions of tonnes tailings are produced yearly
2. modern technology make the exploitation of lower grade ores possible resulting in always inclining amounts

Experimental design

- Focus on Zn, Cu, Ni and Pb by the implementation of an innovative lixiviant: **TEA**
- Results **compared** with **the ammonia based leaching** procedure
  Why? Well understood, widely used lixiviant
  Low toxicity, low cost, easy recovery and high selectivity
- Implementation of TEA:
  Why? Formation of **coordination bonds** with metals must further increase the leaching efficiency of the target metals
  Alkaline character (pka 10.75) = arisen of soluble metal hydroxides.
  Stabilizer in followed MOF synthesis

Analysis requirements

- pH/ORP measurements, ICP-OES analyses, XRF-analyses and XRD-analyses

MOF SYNTHESIS

OBJECTIVES

- Determine **optimal MOF synthesis conditions** starting with synthetic metal salts considering the reaction time, organic linker concentration, TEA concentration, temperature, pH
- Studying the reaction kinetics to form **selectively MOFs** from a mixture of metals
- Synthesize **phase pure MOFs** starting from a mineral waste stream

APPROACH

Scientific background

- Definition: “ A class of **coordination polymers** promising organic linkers wherein metal ligand interaction/bonding leads to 2D or **3D crystalline network** structures” [4]
- A lot of **diversity** is possible in terms of crystal size, porosity, geometry and functionality due to the multiple possible combinations of metallic centres and organic ligands
- As a result of this diversity and their porous, crystalline nature, MOFs can be interest in **several applications** summarized in figure 3 [5]

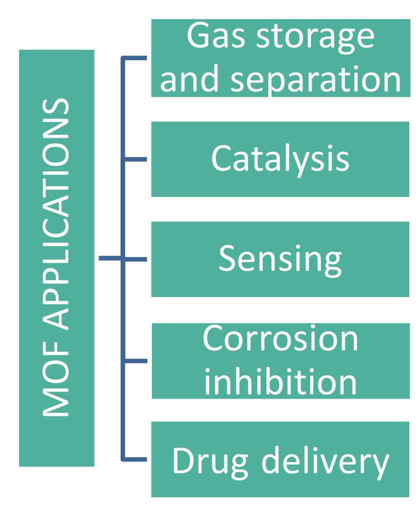

Figure 3. MOF applications

- In this study there is focused on the synthesis of **imidazole based MOFs**, especially Zeolitic imidazole framework 8 (ZIF-8)
- **ZIF-8** is the result of the complexation reaction between the metal cation and the free electrons of nitrogen present in **2-methylimidazole** (Hmim). Hmim consist two available N-donors: one imine N group and one amine NH group [6]

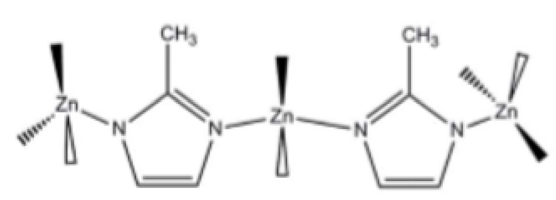

Figure 4. ZIF-8 (p.26)

- Advantages ZIF-8: high chemical resistance & high thermal stability [7]

Experimental design

Table 1. Variating synthesis parameters

Reaction temperature (°C)	20 – 80 – 120
TEA concentration (M)	0 – 30 – 90
Hmim concentration (M)	30 – 90

Analysis requirement

- pH/ORP measurements, ICP-OES analyses, XRF analyses, XRD analyses and SEM analyses

CONCLUSION

This study focusses on an innovative, environmental friendly way to **recycle metals**. An **advanced leaching** method followed by the synthesis of a valuable end-product**, MOFs**, forms the red guideline through the process. Large **opportunities** are possible since the mineral waste stream tailings are produced in abundance. The recovery of **Zn, Cu, Ni and Pb** is the major concern together with avoiding the interfering elements as Ca, Mg, Fe,… Therefore, the reaction kinetics of these metals together with the **novel lixiviant TEA** must be determined to achieve the highest possible leaching efficiency. This first leaching step is crucial in the further development of MOFs. To form these **coordinated structures** the organic linker 2-methylimidazole is implemented ending in imidazole based MOFs.

Also TEA plays an important role by stabilizing the reaction and pulling the conversion the right way. Furthermore an exceptional quality of these imidazole based MOFs is their **chemical resistance** to various solvents. This induces the idea to develop an aqueous synthesis of MOFs. Water forms an **environmental friendly** reaction medium besides large **industrial up-scaling** chances. Once the yield of the whole process is optimized, a lot of **new opportunities** become true. The **crystal formation** can be further investigated to gain a more valuable material adapted to the given MOF application. **Up-scale experiments** can also be examined and will form the main challenge before starting **process optimization** on the field.

Supervisors / Cosupervisors:

Prof. Dr. Ir. Braeken L.
Dr. Ir. Everaert M.

[1] Engels, J;, „tailings.info,” tailings.info, 2020. [Online]. Available: http://www.tailings.info/basics/tailings.htm. [opend 2 April 2020].
[2] M. Pizzol, P. Christensen, J. Schmidt en M. Thomsen, „Impacts of "metals" on human health: a comparison between nine different methodologies for life cycle impact assessment(LCIA),” *Journal of cleaner production,* nr. 19, pp. 646-656, 2011.
[3] P. Breuer, X. Dai en M. I. Jeffrey, „Leaching of gold and copper minerals in cyanide deficient copper solutions,” *Hydrometallurgy,* vol. 78, nr. 3-4, pp. 156-165, 2005.
[4] M. F. Navarro Pouard, E. Polo, P. Taboada, A. Arenas-Vivo, P. Horcajada, B. Pelaz en P. Del Pino, „Aqueous Synthesis of Copper(II)-Imidazolate Nanoparticles,” *Inorganic Chemistry,* vol. 57, nr. 19, pp. 12056-12065, 2018.
[5] D. Alezi, Y. Belmabkhout, M. Suyetin, P. M. Bhatt, L. J. Weselinski, V. Solovyeva, K. Adil, I. Spanopoulos, P. N. Trikalitis, A. Emwas en M. Eddaoudi, „MOF crystal chemistry paving the way of gas storage needs: ALuminum-based soc-MOF for CH4, O2 and CO2 storage,” *Journal of the American chemical society,* nr. 137, pp. 13308-13318, 2015.
[6] M. Jian, B. Liu, R. Liu, J. Qu, H. Wang en X. Zhang, „Water-based synthesis of zeolitic imidazolate framework-8 with high morphology level at room temperature,” *RSC Advances,* nr. 5, pp. 48433-48441, 2015.
[7] L. Jian Bin, L. Rui-Biao, C. Xiao-Ning, Z. Jie-Peng en Z. Xiao-Ming, „Solvent/additive-free synthesis of porous/zeolitic metal azolate frameworks from metal oxide/hydroxide,” *Chemical Communications,* vol. 47, nr. 32, pp. 9185-9187, 2011.

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