9th International Conference
MINING AND ENVIRONMENTAL PROTECTION
May 2023, Serbia

Role of the unit operations in non-ferrous metallurgy for environmental protection

Srecko Stopic, Bernd Friedrich
IME Process Metallurgy and Metal Recycling, RWTH Aachen University, Aachen, Germany,
sstopic@ime-aachen.de

Abstract: Unit operations in non-ferrous extractive metallurgy have high importance for environmental protection. Three categories are included in unit operations in non-ferrous extractive metallurgy: (1) hydrometallurgy (leaching under atmospheric and high pressure conditions, mixing of solution with gas and mechanical parts, neutralization of solution, precipitation and cementation of metals from solution aiming purification, and compound productions during crystallization), (2) pyrometallurgy (roasting, smelting, refining), and (3) electrometallurgy (aqueous electrolysis and molten salt electrolysis). The high demand for critical metals in modern life, such as rare earth elements (REE), indium, scandium, and gallium has highly increased the need for an advance in understanding of an application of the unit operations in non-ferrous metallurgy regarding to an environmental impact. Carbonation of olivine and slag in one closed reactor under high pressure as shown as new strategy to contribute an environmental protection.

Keywords: *non-ferrous metallurgy, unit operations, environmental protection, carbonation*

1. INTRODUCTION

Advances in understanding of a role of the unit operations in non-ferrous metallurgy have high significance in environmental protection. In hydrometallurgy, the aimed metal is first transferred from ores and concentrates to an acidic solution using a selective dissolution (leaching and dry digestion) under an atmospheric pressure below 100 °C and under a high pressure (40-50 bar) and high temperature (below 270°C) in an autoclave and tube reactor [1-5]. The purification of the obtained solution was performed using neutralization agents such as NaOH and $CaCO_3$ or more selective precipitation agents (Na_2CO_3 and oxalic acid) [6-8], as shown at Figure 1.

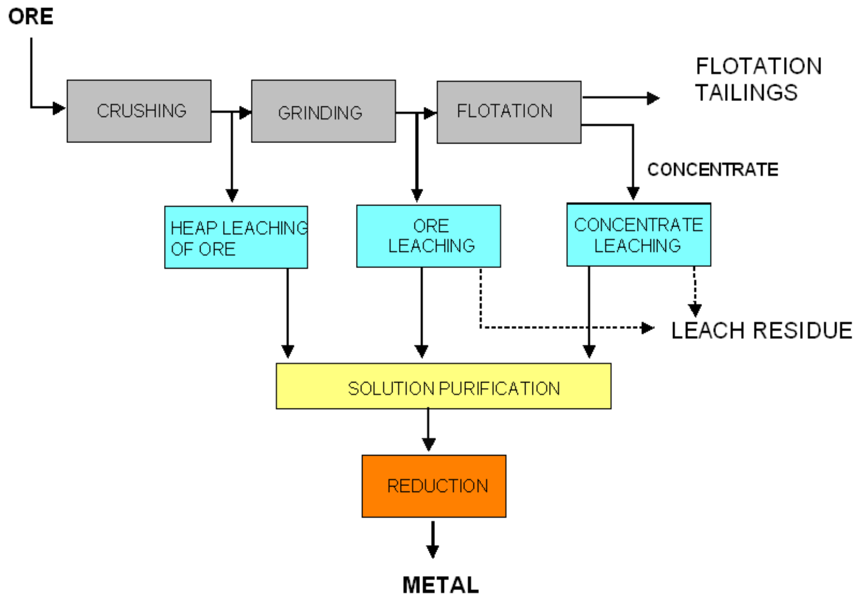

Figure 1. Applications of hydrometallurgical unit operations for metal winning from ores and concentrates

The separation of metals is possible using liquid/liquid process (solvent extraction in mixer-settler) and solid-liquid (filtration using a filter-press under high pressure (approx. 5-6 bar) [9-10]. Crystallization is the process by which a metallic compound is converted from a liquid into a solid crystalline state via a supersaturated solution [11]. The final step is metal production using electrochemical reduction process (aqueous electrolysis for basic metals such as copper, zinc, silver and molten salt electrolysis for rare earth elements and aluminum) [12-15].
Advanced processes, such as ultrasonic spray pyrolysis [16—18] and ultrasound-assisted leaching [19, 20], can be combined with reduction processes in order to produce metallic powders. Some preparation for the leaching process is performed via a roasting process in a rotary furnace, where the sulfidic ore was first oxidized in an oxidic form, which is a suitable for the metal transfer to water solution. During the smelting process, the target metal is further refined at high temperatures and reduced to its pure form. The pyrometallurgical treatment of the ore was performed in an electric furnace and combined with a refining during distillation. Unit Operations in non-ferrous extractive metallurgy can be successfully used for the recovery of non-ferrous metals from secondary materials such as spent NdFeB-magnets [21].
One proposed application of combined hydrometallurgical and pyrometallurgical unit operations in non-ferrous metallurgy is shown at Figure 2.

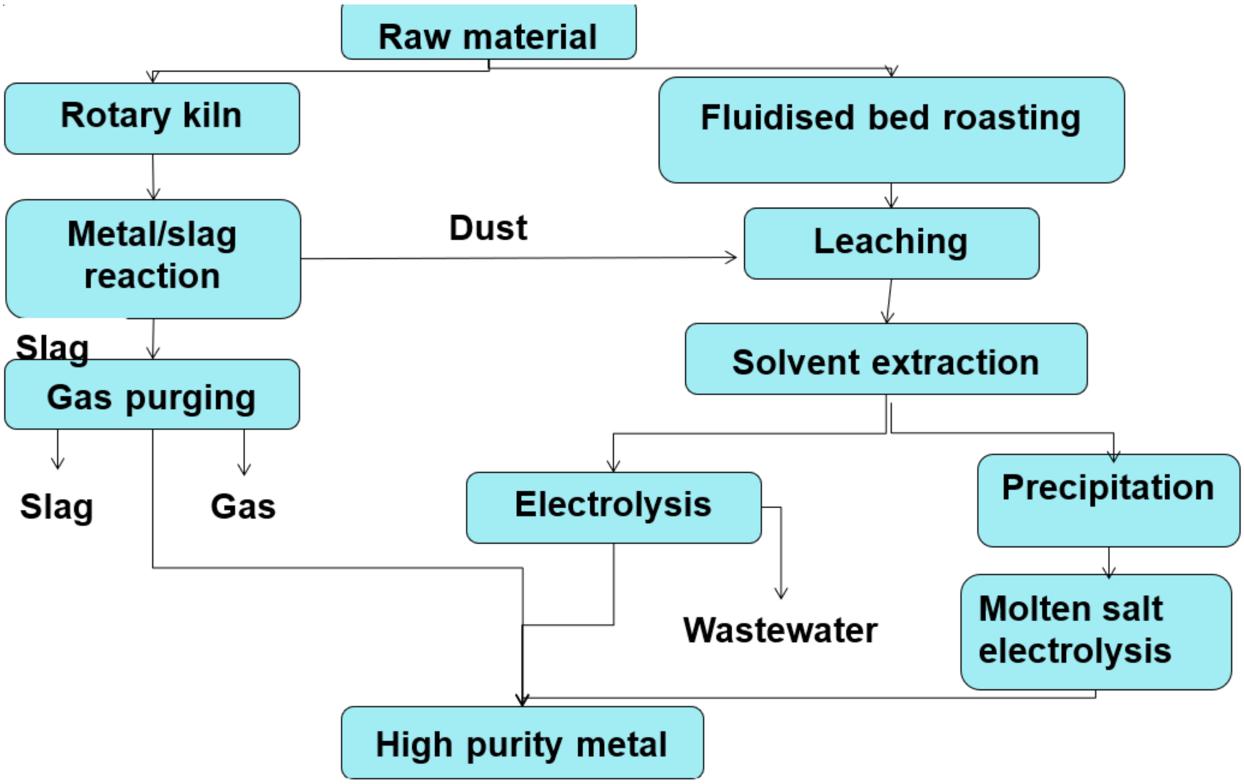

Figure 2. Applications of hydrometallurgical and pyrometallurgical unit operations for metal winning from raw materials in one proposed process

Advantages of hydrometallurgical operations in comparison to pyrometallurgical treatment contain: highly selective reactions, reduced energy consumption, no off gas/flue dusts and economical processing of low grade ores. Some disadvantages of hydrometallurgical operations are present: formation of waste solutions, small grained and wet residue and low reaction velocity. After an analysis of the positive influence of hydrometallurgical operations on environmental protection, carbonation process using olivine and metallurgical slags under high pressure and high temperature in an autoclave was confirmed as a positive example for an environmental protection.

2. CARBONATION PROCESS

The significance of the results coming from greenhouse gas (GHG) emissions to both the atmosphere and our lives has already been urged and is nowadays well-known. Because of the continuous increase of CO_2 concentration in the atmosphere since the industrial revolution, various techniques are proposed.

Carbon capture and utilization (CCU) is considered as the most promising technique in order to use the product in cement industry, transforming it into insoluble carbonate (mainly calcite and magnesite), that is able to remain stable in a geological timeframe. Synthesis of submicron and silica was firstly studied via carbonation of olivine and metallurgical slags in water solution using different size fractions (under 20 µm, between 20 and 63 µm, and between 100 and 200 µm) with different solid/liquid ratios of 1:15 and 1:5 at 175 °C and pressure of CO_2 (70-117 bar) in an autoclave (0.5, 1.0 and 10 L) in the presence and in the absence of additives such hydrogen bicarbonate, oxalic acid and ascorbic acid, as shown at Figure 3,

Figure 3: 1 L autoclave with data collection (1eft) and 10 L autoclave (right)

Scale up operations in an autoclave were performed in the presence and in the absence of the previous mentioned additives in volume of 1170 L using the following parameters. pH: 7.2-8,5¸ Temperature (°C): 175, max pressure: 55 bar (working pressure 30 bar), solid/liquid ratio (1:8) and max fraction: 4 mm, as shown at Figure 4.

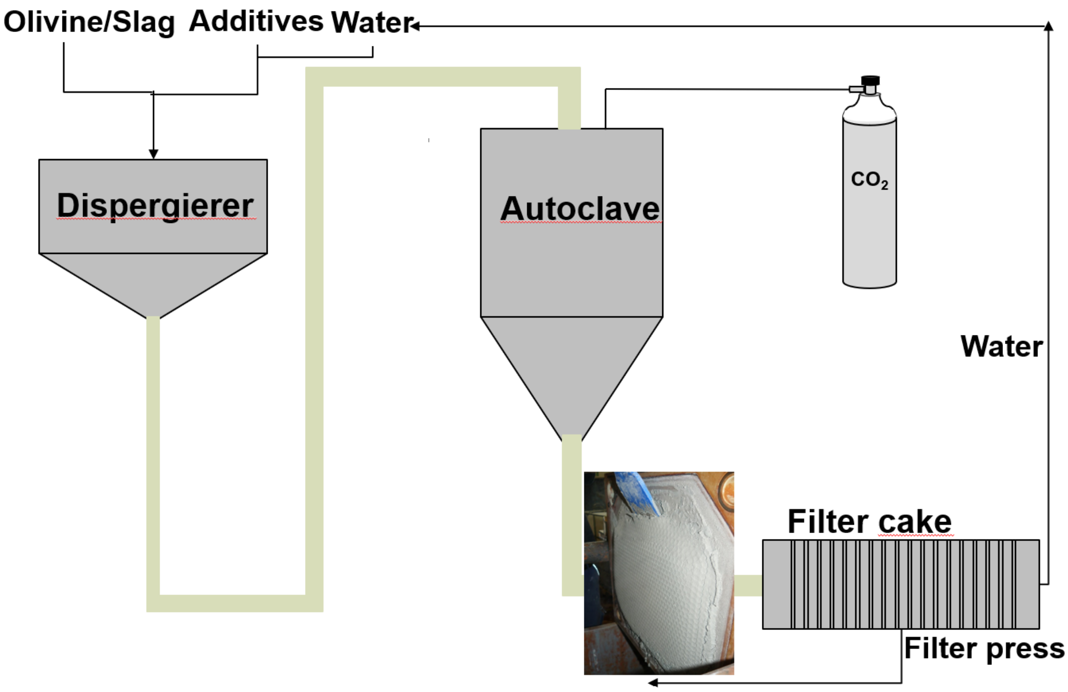

Figure 4. Scale up operation for carbonation process

The used operations contain: mixing of slag and olivine with water, transport of the prepared suspension to autoclave, carbonation process with CO_2 under pressure in an autoclave, and separation of filter cake from water after carbonation using an industrial filter press. The used water in an autoclave after separation in a filter press can be used again in carbonation process. This water is a secondary source for the extraction of nickel, cobalt and magnesium [22, 23]. It is according with zero-waste concept of this study. Comparative analysis of carbonation of olivine and metallurgical slags revealed next findings:

- Maximal carbonation efficiency (360 kg_{CO2}/ t) was reached for an industrial waste such as a slag in ferrochromium production in an electric arc furnace (EAF), what is three time higher than a carbonation of olivine under same conditions, and higher that ladle slag from steel making, as shown at Figure 5.
- Carbonation process of slag is possible in the absence of additives in comparison to olivine

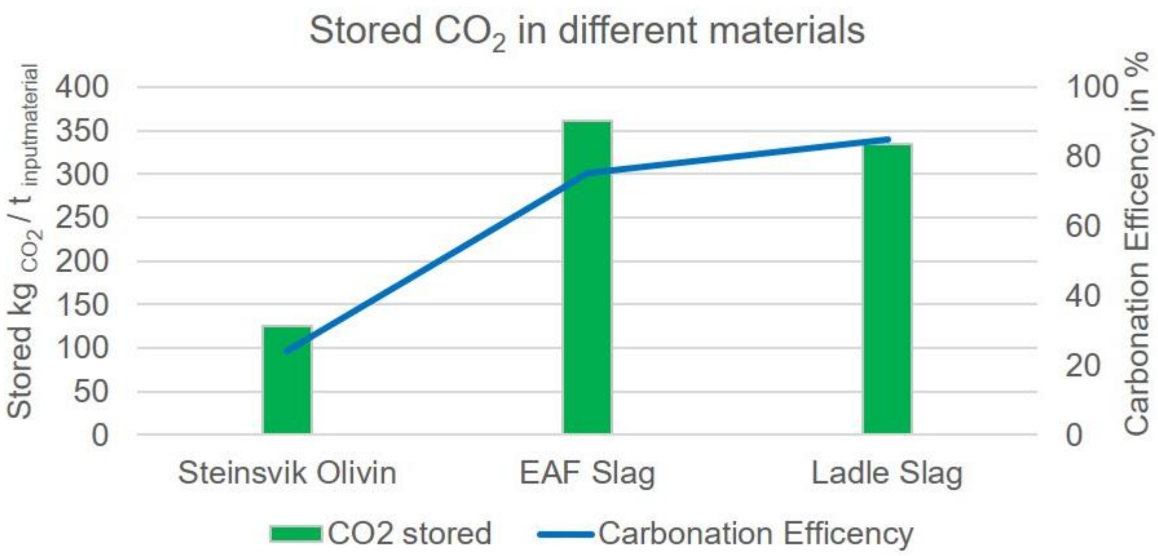

Figure 5. Comparative analysis of the carbonation of olivine and EAF- and ladle slag

CO_2 capturing through mineral raw materials and metallurgical slags in an autoclave enables production of marketable products with simultaneous sequestration.

3. CONCLUSION

In chemical and metallurgical engineering and related fields, a unit operation is a basic step in a process. Unit operations involve a physical change or chemical transformation such as dissolution of materials, separation, crystallization, evaporation, filtration, cementation and electrochemical reduction. Using hydrometallurgical operation enables formation a research strategy for the metal winning from primary and secondary materials. Combination of hydrometallurgical and pyrometallurgical treatment leads to reduction processes for metal winning using aqueous electrolysis or molten salt electrolysis. Carbonation of olivine and secondary materials such as slags, red mud and flying ashes can be new research challenges in order to give high contribution to an environmental protection.

Acknowledgment: This research was funded by BMBF (Federal Ministry of Education and Research) in Berlin, grant number 033RC014B (CO2MIN Project in period from 01.06.2017 to 31.12.2020).

REFERENCES

1. Stopić, S., Friedrich, B, 2018. Leaching of rare earth elements with sulfuric acid from bastnasite ores, Military Technical Courier **2018**, 66(4), pp.757-770. Available at: https://doi.org/10.5937/vojtehg66-17177
2. Stopic, S., Friedrich B. Leaching of rare earth elements from bastnasite ore: Second part, Military Technical Courier **2019**, 67, 2., 241-254; DOI: 10.5937/vojtehg67-20103
3. Stopic, S., Friedrich B. Leaching of rare earth elements from bastnasite ore (third part), Military Technical Courier **2019**, 67, 3, 561-572 DOI: 10.5937/vojtehg67-21153
4. Matus, C., Stopic, S., Friedrich, B. Carbonation of Minerals and Slags under High Pressure in an Autoclave, Military Technical Courier **2021**, 69, 2; DOI: 10.5937/vojtehg69-30203
5. Stopic, S.; Friedrich, B., Advances in Understanding of the Application of Unit Operations in Metallurgy of Rare Earth Elements, Metals **2021**, 11(6), 978, [10.3390/met11060978]
6. Lukas, H., Stopic., Xakalashe, B., Ndlovu, S., Friedrich, B., Synergism Red Mud-Acid Mine Drainage as a Sustainable Solution for Neutralizing and Immobilizing Hazardous Elements, Metals **2021,** 11 (4), 620; https://doi.org/10.3390/met11040620
7. Mitterecker, J., Košević , M., Stopic , S., Friedrich, B., Panić, V., Stevanović, J., Mihailović, M., Electrochemical investigation of lateritic ore leaching solutions for Ni and Co ions extraction, Metals **2022**, *12*(2), 325; https://doi.org/10.3390/met12020325
8. Ma, Y., Stopic, S., Wang, X., Forsberg, K., Friedrich, B: Basic Sulfate Precipitation of Zirconium from Sulfuric Acid Leach Solution, Metals **2020**, 10, 1099. https://doi.org/10.3390/met10081099
9. Alkan, G., Yagmurlu, B., Cakmakoglu, S., Hertel, T., Kaya, S., Gronen, L., Stopic, S., Friedrich, B.: Novel Approach for Enhanced Scandium and Titanium Leaching Efficiency from Bauxite Residue with Suppressed Silica Gel Formation, Nature **2018**, Scientific Reports, 8, 5676, doi: 10.1038/s41598-018-24077-9.
10. Vieceli, N., Vonderstein, C., Swiontek, T., Stopic, S., Dertmann, C., Sojka. R., Reinhardt, N., Ekberg, C., Friedrich, B., Petranikova, M. Recycling of Li-Ion Batteries from Industrial Processing: Upscaled Hydrometallurgical Treatment and Recovery of High Purity Manganese by Solvent Extraction, Solvent Extraction and Ion Exchange **2023**, pp. 1-16. https://www.tandfonline.com/loi/lsei20
11. Kaya, S., Stopic, S., Friedrich, B., Dittrich, C: Concentration and Separation of Scandium from Ni Laterite Ore Processing Streams, Metals **2017**, 7, 557. https://doi.org/10.3390/met7120557
12. Markovic, R. ; Krstic, V. ; Friedrich, B. ; Stopic, S. ; Stevanovic, J. ; Stevanovic, Z. ; Marjanovic, V. Electrorefining Process of the Non-Commercial Copper Anodes,, Metals **2021**, 11(8), 1187, [10.3390/met11081187]
13. Yasinskiy, A. ; Padamata, S. K. ; Moiseenko, I., Stopic, S.; Feldhaus, D. M.; Friedrich, B. ; Polyakov, P. Aluminium Recycling in Single- and Multiple-Capillary Laboratory Electrolysis Cells, Metals **2021**, 11(7), 1053 [10.3390/met11071053]
14. Padamata, S., Yasinskiy, A., Stopic, S., Friedrich, B., Fluorination of two dimensional graphene: Review, Journal of Fluorine Chemistry **2022**, 255–256, 109964, https://doi.org/10.1016/j.jfluchem.2022.109964
15. Cvetković, V.S.; Vukićević, N.M.; Milićević-Neumann, K.; Stopic, S.; Friedrich, B.; Jovićević, J.N. Electrochemical Deposition of Al-Ti Alloys from Equimolar $AlCl_3$ + NaCl Containing Electrochemically Dissolved Titanium, Metals ***2020****, 10, 88,* https://doi.org/10.3390/met10010088

16. Varničić, M. ; Pavlović, M. M. ; Eraković Pantović, S. ; Mihailović, M. ; Pantović-Pavlović, M. R. ; Stopić, S. ; Friedrich, B. Spray-Pyrolytic Tunable Structures of Mn Oxides-Based Composites for Electrocatalytic Activity Improvement in Oxygen Reduction, *Metals* **2022**, 12(1), 22, [10.3390/met12010022]

17. Özcelik, D., Ebin, B., Stopic, S., Gürmen, S., Friedrich, B. Mixed Oxides $NiO/ZnO/Al_2O_3$ Synthesized in a Single Step via Ultrasonic Spray Pyrolysis (USP) Method, Metals **2022**, *12*(1), 73; https://doi.org/10.3390/met12010073

18. Köroğlu, M. ; Ebin, B. ; Stopic, S. ; Gürmen, S. ; Friedrich, B. One Step Production of Silver-Copper (AgCu) Nanoparticles, Metals **2021**, 11(9), 1466 (2021) [10.3390/met11091466]

19. Kießling, F.; Stopic, S.; Gürmen, S.; Friedrich, B. Recovery of Diamond and Cobalt Powder from Polycrystalline Drawing Die Blanks via Ultrasound-Assisted Leaching Process—Part 1: Process Design and Efficiencies, Metals **2020**, *10*, 731, https://doi.org/10.3390/met10060731

20. Kießling, F.; Stopic, S.; Gürmen, S.; Friedrich, B. Recovery of Diamond and Cobalt Powders from Polycrystalline Drawing Die Blanks via Ultrasound Assisted Leaching Process—Part 2: Kinetics and Mechanisms. Metals **2020**, *10*, 741, https://doi.org/10.3390/met10060741

21. Chung, H., Prasakti, L., Stopic, S., Prasakti, L., Cvetkovic, V., Friedrich, B, Recovery of Rare Earth Elements from Spent NdFeB-Magnets: Metal Extraction by Molten Salt Electrolysis (Third Part), Metals **2023**, 13, https://doi.org/10.3390/xxxxx

22. Stopic, S., Dertmann, C., Modolo, G., Kegler, P., Neumeier, S., Kremer, D., Wotruba, H., Etzold, S., Telle, R., Rosani, D, Knops, P., Friedrich, B., Synthesis of Magnesium Carbonate via Carbonation under High Pressure in an Autoclave, Metals **2018**, (12), 993; https://doi.org/10.3390/met8120993

23. Matus, C. Stopic, S., Etzold, S., Kremer, D., Wotruba, H., Dertmann, C., Telle, R., Knops, P., Friedrich, B.: Mechanism of Nickel, Magnesium, and Iron Recovery from Olivine Bearing Ore during Leaching with Hydrochloric Acid Including a Carbonation Pre-Treatment, Metals **2020**, 10, 811, https://doi.org/10.3390/met10060811