



# **Separation Techniques for the Efficient and Green Recovery of Metal Minerals**

Hongtao Chang<sup>1</sup> and Guoquan Zhang<sup>2,\*</sup>

- <sup>1</sup> College of Materials and Metallurgy, Inner Mongolia University of Science & Technology, Baotou 014010, China; cht158@163.com
- <sup>2</sup> School of Chemical Engineering, Sichuan University, Chengdu 610065, China
- Correspondence: zhanggq@scu.edu.cn

# 1. Introduction

In 2022~2023, eight high-quality papers were published in the Special Issue of *Separations* entitled "Efficient and Green Recovery of Metal Minerals". Traditionally, the term mineral resources refers to the collection of minerals or useful elements formed through geological mineralization. With the continuous exploitation of mineral resources, the availability of rich or easily extractable minerals is progressively diminishing. People are turning to the efficient development of lean and secondary metal resources [1–4]. Our Editorial Board noticed that while the previously mentioned eight papers focus on the extraction of metals from minerals, some also investigate the reuse of metals from waste secondary resources. In this Special Issue, the efficient and green separation of Li, Co, Ni, Mn, Ti, V, and other non-ferrous metal resources is comprehensively discussed.

There are two conventional methods for separating non-ferrous metals: pyrometallurgy and hydrometallurgy. The essence of the pyrometallurgical process is the application of physical and chemical principles in chemical reactions at high temperatures, while the hydrometallurgical process consists of the large-scale application of aqueous solution chemistry or electro-chemistry. The reactions occurring in pyrometallurgical processes, including reduction, oxidation, decomposition, sulfurization, halogenation, distillation, distribution, etc., offer the advantages of fast reaction speeds, short processes, and less equipment [5]. The hydrometallurgy process usually includes three main steps, namely, leaching, purification, and sedimentation, which can efficiently separate metals from polymetallic-coexisting or lean ores [6].

In order to improve metal recovery rates, researchers occasionally employ a process combining pyrometallurgy and hydrometallurgy, such as that used in the extraction of vanadium from vanadium slag. Vanadium slag is one of the secondary resources of vanadium titanium magnetite. Vanadium slag contains valuable metals such as vanadium, titanium, iron, manganese, and chromium [7]. Individual pyrometallurgical or hydrometallurgical technologies cannot be used to separate the valuable metals mentioned above simultaneously. As the vanadium-containing phase in vanadium slag is a vanadium iron spinel structure, which has a complex lattice structure, it is difficult to efficiently extract vanadium using only the leaching process [8]. Researchers have developed sodium-roasting waterleaching and calcium-roasting acid-leaching processes for vanadium extraction. These processes consist of using NaCl or CaCl<sub>2</sub> as an additive when roasting vanadium slag at 850 °C and then leaching the roasted slag using water or  $H_2SO_4$  [9].

The efficient and green recovery of metal minerals is a timeless topic. The efficient utilization of mineral resources is crucial for the development of modern economies and society. As traditional fossil fuels become increasingly depleted, attention is turning to solar, wind, nuclear, and hydrogen energy. However, the foundation for the development of these new energy technologies is based on the efficient utilization of mineral resources. Perovskite is a research hotspot in the field of solar energy, and the structures and properties of metal



Citation: Chang, H.; Zhang, G. Separation Techniques for the Efficient and Green Recovery of Metal Minerals. *Separations* **2023**, *10*, 520. https://doi.org/10.3390/ separations10100520

Received: 11 August 2023 Accepted: 12 September 2023 Published: 25 September 2023



**Copyright:** © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). oxides constitute one of the main topics discussed is in this regard [10]. How to prepare pure metal oxides is an issue concerning the efficient utilization of mineral resources [11]. Large wind-power generation equipment should be equipped with high-performance wind turbines, whose performance and efficiency depend on the use of neodymium, praseodymium, and dysprosium and other rare earth elements [12–14]. Improving the distribution ratio and separation coefficients of these rare earth elements is one of the important research areas for rare earth minerals. The development of nuclear energy is based on the efficient separation of radioactive metal elements. Radioisotope separation is also an issue regarding the efficient utilization of mineral resources [15,16]. Furthermore, the safe storage and efficient preparation of hydrogen energy are closely related to the research and development of advanced metal materials. Common hydrogen storage alloys include rare earth series, zirconium series, iron titanium series, magnesium series, etc. [17–19]. These alloy elements are also extracted from mineral resources.

Whether it is the optimization of metal separation processes, the design of separation reaction equipment, or the preparation of alloy materials through metal separation, they are all popular topics in our journal. In this Special Issue of *Separations* titled "Efficient and Green Recovery of Metal Minerals", researchers discuss selective extraction processes, scale up experiments for separation processes, perform separation in rotating flow fields, and determine separation mechanisms. This Special Issue also contains a review paper concerning the separation of magnesium and lithium in salt lake brine. This Editorial aims to increase the visibility of this Special Issue and encourage scholars to publish articles about metal separation in our journal.

#### 2. Summary of Published Articles

Lithium-ion batteries used in new energy vehicles have a lifespan of 5–8 years. With the large-scale use of new energy vehicles, waste lithium-ion batteries are attracting an increasing amount of attention [20–23]. Common types of lithium-ion batteries include ternary material batteries and lithium iron phosphate batteries. The power performance of ternary material batteries is superior, but the addition of elements such as nickel, cobalt, and manganese results in high usage costs. Waste lithium-ion batteries contain a large amount of valuable metal elements, such as Li, Co, Ni, and Mn. The traditional methods for recycling waste lithium-ion batteries mainly involve the use of sulfuric acid leaching and precipitation processes. In order to reduce the amount of waste acid polluting the environment, Kun wang et al. proposed the use of an organic acid to leach spent lithiumion batteries. They used 2 M acetic acid, 4.0 vol.%  $H_2O_2$ , to leach spent batteries in a solid–liquid ratio of 20 g/L each at 70 °C for 40 min. The results showed that the leaching rates of lithium, cobalt, nickel, manganese, and aluminum reached 98.56%, 94.61%, 96.39%, 97.97%, and 94.7%, respectively [24]. Furthermore, due to the surge in the demand for lithium resources, researchers have further developed lithium extraction technologies using salt lake brine. Yueyu Liu presents a review of MOF nanofiltration membranes used in the separation of Li from salt lake brine [25].

In order to improve reaction efficiency, chemical production processes require the use of catalysts with good catalytic performance. However, impurities in the reaction process may react with the catalyst and precipitate its failure. Junbo Zhou proposed using roasting and leaching processes to recover Ni, Co, Mo, and V from a waste hydrodesulfurization (HDS) catalyst. The results showed that 93.9% of Ni, 100.0% of Co, 99.8% of Mo, and 92.8% of V could be recovered. Furthermore, they used recycled metal to remake LiNi<sub>0.533</sub>Co<sub>0.193</sub>Mn<sub>0.260</sub>V<sub>0.003</sub>Fe<sub>0.007</sub>Al<sub>0.004</sub>O<sub>2</sub> battery cathode materials, which showed excellent electrochemical performance [26].

This Special Issue includes two papers discussing the comprehensive utilization of vanadium and titanium resources. One research team proposed the incorporation of ammonium sulfate in the roasting of vanadium slag. Using FT-IR, XRD, XPS, and SEM techniques, they showed the result of the decomposition and transformation of vanadium slag during ammonium salt roasting, revealing that Fe, V, Ti, and Mn transformed

into sulfate, with some of these elements presenting changes in chemical valence [27]. Titanium dioxide waste acid is a waste acid produced using the sulfuric acid method in the production of titanium dioxide [28]. Another research team discussed a new process for treating titanium dioxide waste acid. In addition to sulfuric acid, titanium dioxide waste acid contains a large amount of ferrous sulfate, which hinders the development of the titanium dioxide industry. This research team proposed using a new technique consisting of step extraction and the comprehensive utilization of titanium dioxide waste acid. They removed other impurities in the form of phosphates when iron was in a reduced state. If the iron was in the Fe(III) form, iron phosphate was formed [29].

The use of external metallurgical techniques such as microwave, ultrasound, and supergravity methods may further enhance metal extraction. Long Wang published a paper discussing the extraction of Re, Ni, Co, Al, and Cr from superalloy scraps via an ultrasonic leaching method. They found that 92.3% Re, 95.2% Ni, 98.5% Co, 98.7% Al, and 97.5% Cr could be extracted in the ultrasonic leaching process, corresponding to an about 20% improvement in the leaching rate compared to that of the conventional leaching process [30]. Chunwei Shi discussed the degradation of azo dye via ultrasound in a rotating flow field. Azo dyes are carcinogenic substances. Thus, it is necessary to explore their degradation processes. The authors found that using a combination of ultrasound and mechanical stirring led to an efficient degradation of the azo concentration in a solution without requiring the frequent supplementation of ferrous chloride solution [31].

The successful promotion of laboratory technology to industrial applications has always been a dream for researchers. The depletion of aluminum resources has led to increasing attention to the development of low-grade bauxite mines. Yang Chen extracted Al from low-grade bauxite on a semi-industrial experiment scale. Using the calcification–carbonization method for processing low-grade alumina, they found that only 0.95% Na<sub>2</sub>O was left in the bauxite residue, while only 0.85 A/S was present in the final red mud. The total Al dissolution rate could reach over 80% [32–34].

## 3. Conclusions

The articles published in this Special Issue of *Separations*, titled "Efficient and Green Recovery of Metal Minerals", cover topics ranging from the recycling of spent lithium-ion batteries and catalysts to the efficient utilization of vanadium and titanium resources, the scaling up of experiments for low-grade bauxite, and Azo degradation and rare metal extraction using ultrasound. These studies reveal that Li, Co, Ni, and Mn in spent lithium-ion batteries can be recovered via organic acid leaching processes. Mo, V, Ni, and Co in waste catalysts can be reused as synthetic cathode materials for lithium batteries. Calcification and carbonization methods can facilitate the large-scale dissolution of low-grade bauxite aluminum. Using ultrasound technologies, the efficient degradation of azo fuel and the extraction of rare metals can be achieved. Furthermore, the included review paper may provide insight into the application of MOF nanofiltration membranes to the separation of Mg and Li from salt lakes.

Author Contributions: H.C.: investigation and writing—original draft. G.Z.: funding acquisition and guidance. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the National Natural Science Foundation of China (22008161).

Conflicts of Interest: The authors declare no conflict of interest.

## References

- Chang, C.; Guan, X.; Wang, P.; Zhou, X.; Xie, X.; Ye, Y. Electrically and thermally conductive Al<sub>2</sub>O<sub>3</sub>/C nanofiber membrane filled with organosilicon as a multifunctional integrated interlayer for lithium-sulfur batteries under lean-electrolyte and thermal gradient. *Chem. Eng. J.* 2022, 442, 135825. [CrossRef]
- Kaya, M.; Hussaini, S.; Kursunoglu, S. Critical review on secondary zinc resources and their recycling technologies. *Hydrometallurgy* 2020, 195, 105362. [CrossRef]

- 3. Dhawan, N.; Tanvar, H. A critical review of end-of-life fluorescent lamps recycling for recovery of rare earth values. *Sustain. Mater. Techno* **2022**, *32*, e00401. [CrossRef]
- Kanari, N.; Allain, E.; Joussemet, R.; Mochon, J.; Ruiz-Bustinza, I.; Gaballah, I. An overview study of chlorination reactions applied to the primary extraction and recycling of metals and to the synthesis of new reagents. *Thermochim. Acta* 2009, 495, 42–50. [CrossRef]
- 5. Kellogg, H.H.; Rao, Y.K.; Marcuson, S.W. Pyrometallurgy. Annu. Rev. Phys. Chem. 1976, 27, 387–406. [CrossRef]
- Jia, L.; Huang, J.; Ma, Z.; Liu, X.; Chen, X.; Li, J.; He, L.; Zhao, Z. Research and development trends of hydrometallurgy: An overview based on Hydrometallurgy literature from 1975 to 2019. *Trans. Nonferrous Met. Soc. China* 2020, 30, 3147–3160. [CrossRef]
- 7. Zhang, G.; Hu, T.; Liao, W.; Ma, X. An energy-efficient process of leaching vanadium from roasted tablet of ammonium sulfate, vanadium slag and silica. *J. Environ. Chem. Eng.* **2021**, *9*, 105332. [CrossRef]
- 8. Lee, J.; Kurniawan; Kim, E.; Chung, K.W.; Kim, R.; Jeon, H. A review on the metallurgical recycling of vanadium from slags: Towards a sustainable vanadium production. *J. Mater. Res. Technol.* **2021**, *12*, 343–364. [CrossRef]
- Chen, L.; Diao, J.; Wang, G.; Qiao, Y.; Xie, B. Experimental study on slag splashing with modified vanadium slag. *Ironmak*. *Steelmak*. 2019, 46, 165–168. [CrossRef]
- He, T.; Jiang, Y.; Xing, X.; Yuan, M. Structured Perovskite Light Absorbers for Efficient and Stable Photovoltaics. *Adv. Mater.* 2020, 32, 1903937. [CrossRef]
- Liu, P.; Han, N.; Wang, W.; Ran, R.; Zhou, W.; Shao, Z. High-Quality Ruddlesden-Popper Perovskite Film Formation for High-Performance Perovskite Solar Cells. *Adv. Mater.* 2021, *33*, 2002582. [CrossRef] [PubMed]
- 12. Adedipe, O.; Brennan, F.; Kolios, A. Review of corrosion fatigue in offshore structures: Present status and challenges in the offshore wind sector. *Renew. Sust. Energy Rev.* 2016, *61*, 141–154. [CrossRef]
- Ahuir-Torres, J.I.; Bausch, N.; Farrar, A.; Webb, S.; Simandjuntak, S.; Nash, A.; Thomas, B.; Muna, J.; Jonsson, C.; Mathew, D. Benchmarking parameters for remote electrochemical corrosion detection and monitoring of offshore wind turbine structures. *Wind. Energy* 2019, 22, 857–876. [CrossRef]
- 14. Huang, Y.; Wang, D.; Duan, Z.; Liu, J.; Cao, Y.; Peng, W. A Novel Dissolution and Synchronous Extraction of Rare Earth Elements from Bastnaesite by a Functionalized Ionic Liquid [Hbet][Tf2N]. *Minerals* **2022**, *12*, 1592. [CrossRef]
- 15. Kim, J.; Tsouris, C.; Mayes, R.T.; Oyola, Y.; Saito, T.; Janke, C.J.; Dai, S.; Schneider, E.; Sachde, D. Recovery of Uranium from Seawater: A Review of Current Status and Future Research Needs. *Sep. Sci. Technol.* **2013**, *48*, 367–387. [CrossRef]
- 16. Rao, T.P.; Metilda, P.; Gladis, J.M. Preconcentration techniques for uranium(VI) and thorium(IV) prior to analytical determination— An overview. *Talanta* **2006**, *68*, 1047–1064. [CrossRef]
- Faye, O.; Szpunar, J.; Eduok, U. A critical review on the current technologies for the generation, storage, and transportation of hydrogen. *Int. J. Hydrogen Energy* 2022, 47, 13771–13802. [CrossRef]
- Lin, H.; Lu, Y.; Zhang, L.; Liu, H.; Edalati, K.; Revesz, A. Recent advances in metastable alloys for hydrogen storage: A review. *Rare Met.* 2022, 41, 1797–1817. [CrossRef]
- Yang, F.; Wang, J.; Zhang, Y.; Wu, Z.; Zhang, Z.; Zhao, F.; Huot, J.; Novakovic, J.G.; Novakovic, N. Recent progress on the development of high entropy alloys (HEAs) for solid hydrogen storage: A review. *Int. J. Hydrogen Energy* 2022, 47, 11236–11249. [CrossRef]
- Wang, K.; Zhang, G.; Luo, M.; Li, J. Separation of metals from acetic acid leaching solution of spent lithium-ion batteries by ionic liquid system. *Chem. Eng. J.* 2023, 472, 145006. [CrossRef]
- Yao, Y.; Zhu, M.; Zhao, Z.; Tong, B.; Fan, Y.; Hua, Z. Hydrometallurgical Processes for Recycling Spent Lithium-Ion Batteries: A Critical Review. ACS Sustain. Chem. Eng. 2018, 6, 13611–13627. [CrossRef]
- Huang, B.; Pan, Z.; Su, X.; An, L. Recycling of lithium-ion batteries: Recent advances and perspectives. J. Power Sources 2018, 399, 274–286. [CrossRef]
- Gu, F.; Guo, J.; Yao, X.; Summers, P.A.; Widijatmoko, S.D.; Hall, P. An investigation of the current status of recycling spent lithium-ion batteries from consumer electronics in China. J. Clean. Prod. 2017, 161, 765–780. [CrossRef]
- Wang, K.; Zhang, G.; Luo, M. Recovery of Valuable Metals from Cathode—Anode Mixed Materials of Spent Lithium-Ion Batteries Using Organic Acids. Separations 2022, 9, 259. [CrossRef]
- 25. Liu, Y.; Zhu, R.; Srinivasakannan, C.; Li, T.; Li, S.; Yin, S.; Zhang, L. Application of Nanofiltration Membrane Based on Metal-Organic Frameworks (MOFs) in the Separation of Magnesium and Lithium from Salt Lakes. *Separations* **2022**, *9*, 344. [CrossRef]
- Zhou, J.; Qiu, L.; Li, Y.; Deng, Y.; Zhao, Q.; Hu, Y.; Guo, F.; Zhu, C.; Zhong, B.; Song, Y.; et al. High Value-Added Utilization of Waste Hydrodesulfurization Catalysts: Low-Cost Synthesis of Cathode Materials for Lithium-Ion Batteries. *Separations* 2022, 9, 449. [CrossRef]
- 27. Zhang, G.; Wang, K.; Luo, M. Mechanism on the Separation of Vanadium and Titanium from Vanadium Slag by Roasting with Ammonium Sulfate. *Separations* **2022**, *9*, 196. [CrossRef]
- 28. Ma, G.; Cheng, M. Experimental study on preparation of titanium-rich material by pressure leaching of titanium concentrate from titanium dioxide waste acid. *Ferroelectrics* **2021**, *581*, 281–286. [CrossRef]
- 29. Cao, X.; Chen, Y.; Liang, X.; Li, Y.; Zhang, W.; Cai, Z.; Zhang, T.A. Basic Research on Selective Extraction of Iron from Titanium Dioxide Waste Acid to Prepare Iron Phosphate Precursors. *Separations* **2023**, *10*, 400. [CrossRef]
- Wang, L.; Lu, S.; Fan, J.; Ma, Y.; Zhang, J.; Wang, S.; Pei, X.; Sun, Y.; Lv, G.; Zhang, T. Recovery of Rare Metals from Superalloy Scraps by an Ultrasonic Leaching Method with a Two-Stage Separation Process. *Separations* 2022, *9*, 184. [CrossRef]

- 31. Shi, C.; Yang, F.; Qu, X. Degradation of Azo Dye by Ultrasound in Rotating Flow Field. Separations 2023, 10, 321. [CrossRef]
- 32. Chen, Y.; Long, F.; Cao, X.; Li, Y.; Zhang, W.; Zhang, T.; Lv, G. Exploration of Large-Scale Application of Efficient and Clean Utilization of Low-Grade Bauxite. *Separations* **2023**, *10*, 336. [CrossRef]
- 33. Lu, G.; Zhang, T.; Ma, L.; Wang, Y.; Zhang, W.; Zhang, Z.; Wang, L. Utilization of Bayer red mud by a calcification-carbonation method using calcium aluminate hydrate as a calcium source. *Hydrometallurgy* **2019**, *188*, 248–255. [CrossRef]
- 34. Wang, Y.; Zhang, T.; Lyu, G.; Guo, F.; Zhang, W.; Zhang, Y. Recovery of alkali and alumina from bauxite residue (red mud) and complete reuse of the treated residue. *J. Clean. Prod.* **2018**, *188*, 456–465. [CrossRef]

**Disclaimer/Publisher's Note:** The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.