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Editorial

Advances in Understanding of Unit Operations in Non-Ferrous Extractive Metallurgy in 2023

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Abstract: Metallic materials play a vital role in the economic life of modern societies; hence, research contributions are sought on fresh developments that enhance our understanding of the fundamental aspects of the relationships between processing, properties, and microstructures. Disciplines in the metallurgical field ranging from processing, mechanical behavior, phase transitions, microstructural evolution, and nanostructures, as well as unique metallic properties, inspire general and scholarly interest among the scientific community. Three of the most important elements are included in unit operations in non-ferrous extractive metallurgy: (1) hydrometallurgy (leaching under atmospheric and high-pressure conditions, mixing of a solution with a gas and mechanical parts, neutralization of a solution, precipitation and cementation of metals from a solution aiming at purification, and compound productions during crystallization), (2) pyrometallurgy (roasting, smelting, and refining), and (3) electrometallurgy (aqueous electrolysis and molten salt electrolysis). Advances in our understanding of unit operations in non-ferrous extractive metallurgy are required to develop new research strategies for the treatment of primary and secondary materials and their application in industry.

Keywords: hydrometallurgy; pyrometallurgy; metals; powders

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1. Introduction

The first volume of this Special Issue, "Advances in Understanding of Unit Operations in Non-ferrous Extractive Metallurgy 2021" contains 17 papers divided into six groups (prepared between 1 July 2020 and 31 January 2022) as follows:

1. Roasting (Thermal Decomposition and Kinetics of Pentlandite-Bearing Ore Oxidation in the Air Atmosphere [1]).
2. Leaching (1. Processing Tests, Adjusted Cost Models and the Economies of Reprocessing Copper Mine Tailings in Chile [2]; 2. NdFeB Magnets Recycling Process: An Alternative Method to Produce Mixed Rare Earth Oxide from Scrap NdFeB Magnets; and 3. Advances in Understanding of the Application of Unit Operations in Metallurgy of Rare Earth Elements).
3. Purification of solutions during adsorption, precipitation, and neutralization (1. Selenate Adsorption from Water Using the Hydrous Iron Oxide-Impregnated Hybrid Polymer [3]; 2. Synergism Red Mud-Acid Mine Drainage as a Sustainable Solution for Neutralizing and Immobilizing Hazardous Elements; and 3. Basic Sulfate Precipitation of Zirconium from Sulfuric Acid Leach Solution).
4. Electrochemical methods for metal refining and winning (1. Electrorefining Process of the Non-Commercial Copper Anodes; 2. Aluminium Recycling in Single- and Multiple-Capillary Laboratory Electrolysis Cells; and 3. Electrochemical Investigation of Lateritic Ore Leaching Solutions for Ni and Co Ions Extraction).
5. Synthesis of metallic, oxidic, and composite methods using different processes (1. One Step Production of Silver-Copper (AgCu) Nanoparticles; 2. Synthesis of Silica Particles Using Ultrasonic Spray Pyrolysis Method; 3. Atomic Layer Deposition of a

TiO_2 Layer on Nitinol and Its Corrosion Resistance in a Simulated Body Fluid [4]; 4. Spray-Pyrolytic Tunable Structures of Mn Oxides-Based Composites for Electrocatalytic Activity Improvement in Oxygen Reduction; 5. Mixed Oxides NiO/ZnO/Al_2O_3 Synthesized in a Single Step via Ultrasonic Spray Pyrolysis (USP) Method; and 6. Synthesis and Characterization of a Metal Catalyst prepared by Ultrasonic Spray Pyrolysis as Pre-Definition Step for Titanium oxide-supported Platinum).

6. Characterization and behavior of the produced materials (Microstructural and Cavitation Erosion Behavior of the CuAlNi Shape Memory Alloy).

2. Review of Second Volume

The second volume of this Special Issue, "Advances in Understanding of Unit Operations in Non-Ferrous Extractive Metallurgy in 2023" contains 10 papers divided into six groups (prepared between 1 July 2022 and 30 November 2023). This is presented at the followed link: https://www.mdpi.com/journal/metals/special_issues/Cheryl_understanding_unit_operations_non_ferrous_extractive_metallurgy_2023. The following unit operations are presented via different papers, as shown below:

1. Roasting (Recovery of Rare Earth Elements through Spent NdFeB Magnet Oxidation (Part I)). Due to their remarkable magnetic properties, such as a high maximum energy product, high remanence, and high coercivity, NdFeB magnets are used in a variety of technological applications. Because of their very limited recycling, large numbers of spent NdFeB magnets are widely available on the market. In addition to China's monopoly on the supply of most rare earth elements, there is a need for the recovery of these critical metals, as their high import price poses an economic and environmental challenge for manufacturers. This paper proposes a pyrometallurgical recycling method for end-of-life NdFeB magnets by oxidizing them in air as an initial indispensable step. The main goal of this method is to oxidize rare earth elements from NdFeB magnets in order to prepare them for the carbothermic reduction. The experimental conditions, such as the oxidation temperature and time, were studied in order to establish the phase transformation during oxidation using the Factsage Database. The thermogravimetric TGA analysis revealed an increased sample mass by 35% between room temperature and 1100 °C, which is very close to the total calculated theoretical value of oxygen (36.8% for all elements, and only 3.6% for rare earth elements, REE), confirming the complete oxidation of the material. The obtained quantitative analysis of the oxidation product, in (%), demonstrated values of 53.41 Fe_2O_3, 10.37 Fe_3O_4; 16.45 $NdFeO_3$; 0.45 Nd_2O_3, 1.28 Dy_2O_3, 1.07 Pr_2O_3, and 5.22 α-Fe.
2. Smelting (Recovery of Rare Earth Elements from Spent NdFeB Magnets: Separation of Iron through Reductive Smelting of the Oxidized Material (Part II) and the Feasibility of Recovering Valuable and Toxic Metals from Copper Slag Using Iron-Containing Additives). This second part proposes a pyrometallurgical recycling method for end-of-life NdFeB magnets by oxidizing them in air and subsequently smelting them. The smelting process enables the recovery of rare earth elements (REEs), producing a newly attained concentrate separating the iron as the metallic phase. From the products of smelting, the metallic phase showed a maximum Fe content of 92.3 wt.%, while the slag phase showed a maximum total REE (Nd, Pr, and Dy) content of 47.47 wt.%, both at a smelting temperature of 1500 °C. ICE-OES and XRD analysis were conducted on both phases, and the results showed that the metal phase consists mainly of Fe and Fe_3C, while the slag phase consists of the RE oxides, leftover Fe_2O_3, and a mixture of Fe_6Nd_4. The obtained slag concentrate, based on the oxides of rare earth elements, is suitable for further pyrometallurgical or hydrometallurgical treatment in order to obtain rare earth elements. One of the greatest environmental challenges in metal extraction is the generation of a large amount of slag. Most of these slags contain insufficient amounts of valuable metals for economical revalorization, but these concentrations may be harmful for the environment. At present, more

than 80% of global copper products are obtained via a smelting process, where the major by-products are various slags containing a broad range of almost all known elements. In this study, valuable and potentially harmful elements were recovered from mining waste using gravity separation and gravity settling. The settling process was enhanced by injecting coke, ferrocarbon, ferrosilicon, and ferrosulfide. In total, 35 elements were detected in the samples using electron probe microanalysis. After the treatment, 89.4% of the valuable, toxic, and trace elements gathered in the newly formed matte after maintaining the copper slag for four hours at 1300 °C and adding ferrosilicon. The metallic constituents of slags may be an important source of raw materials and they may come to be considered an environmentally beneficial source of copper and other materials. The suggested practices can prevent harmful elements from entering the environment, generate value from the gathered metals, and make the remaining slag suitable for construction or mine backfill materials. The present article also assesses the challenges in slag processing by the pyrometallurgical route and provides a roadmap for further investigations and large-scale studies.

3. Leaching (1. Options for Hydrometallurgical Treatment of Ni-Co Lateritic Ores for Sustainable Supply of Nickel and Cobalt for the European Battery Industry from Southeastern Europe and Turkey; and 2. A Multifocal Study Investigation of Pyrolyzed Printed Circuit Board Leaching). Following the production of slag, a leaching process is required for the recovery of valuable metals. The automotive industry is undergoing a transformation from the production of traditional vehicles with engines powered by the combustion of fossil fuels to vehicles powered by electric energy. This revolutionary transformation will generate a growing demand for metallic raw materials that are a crucial part of batteries—nickel and cobalt—among others. Providing sufficient quantities of raw materials for e-mobility in a sustainable manner will be a challenge in the years to come. The region of Southeastern Europe (SEE), including Turkey, is relatively rich in lateritic Ni-Co deposits, and this region has the potential to partially replace the import of nickel and cobalt intermediates to the European Union from distant overseas locations. The possibilities for the sustainable sourcing of nickel and cobalt from the SEE region are reviewed in this paper, with overviews of the global demand and production of these metals, the lateritic mineral resources of SEE, the current status of production, and the prospective development of nickel and cobalt production in this region. Most electronic waste from various devices that are disposed of every day contains some form of printed circuit board, the components of which comprise precious and valuable metals. In order to extract these metals, the printed circuit boards used for this study were crushed and pyrolyzed into powder. The fine pyrolyzed printed circuit board (PPCB) powder was separated into fractions, and the fine metallic fraction was used as a raw material for metal leaching extraction. In order to better understand how various metal species react in leaching media, several leaching agents were used (sulfuric acid, nitric acid, glycine, and acid mine drainage, AMD) either alone or with the addition of hydrogen peroxide. Additionally, the influence of the S/L ratio and leaching temperature were investigated in sulfuric acid leaching solutions, as this is currently one of the most widely used methods. In one case, the reactor was heated in a thermal bath, while in the other, it was heated in an ultrasonic bath. Lastly, several experiments were conducted with a (consecutive) two-pronged leaching approach, with and without applied pretreatment. The aim of this paper is to give a multifocal and detailed approach to how metals such as Al, Cu, Co, Zn, Sn, and Ca behave when extracted from fine PPCB powder. However, some attention is also paid to Nd, Pd, Pb, and Ba. One of the main findings is that, regardless of the pretreatment or the sequence of leaching media applied, consecutive two-pronged leaching cannot be used for selective metal extraction. However, AMD was found to be suitable for selective leaching for very limited applications.
4. Purification of solutions during anodic oxidation, precipitation, and neutralization (1. Research of the Process of Purification of a Sulfate Zinc Solution from Iron Ions

Using Anodic Oxidation; and 2. Influence of Process Parameters in Three-Stage Purification of an Aluminate Solution and Aluminum Hydroxide). Following leaching and filtration, the purification of a solution is necessary in order to obtain clean solution for metal recovery. This study considers the possibility of using a membrane electrolytic cell for the electrochemical oxidation of Fe(II) and the purification of real industrial solutions obtained through the atmospheric leaching of low-grade zinc concentrates [5]. The average indicators for carrying out the electrooxidation process are given. Also considered is the possibility of conditioning a zinc sulfate solution by hydrolytic purification with preliminary oxidation of iron in a membrane electrolytic cell with an anion-exchange membrane MA-41 TU 2255-062-05761695-2009. Carrying out direct electrooxidation of iron (II) in sulfate zinc solutions in the anode chamber of a flow membrane electrolyzer ensures good filterability of precipitates after hydrolytic precipitation of iron, since this solution does not contain Fe(II) ions, the presence of which leads to significant difficulties in the operations of separating solid and liquid phases. This makes it possible to exclude the thickening operation from the technological scheme. The degree of oxidation of the iron during the test period was 99.8–99.9%. The residual concentration of iron after precipitation in the form of oxide and hydroxide compounds from the solutions obtained after electrochemical oxidation was less than 0.01 g/dm^3. The influence of process parameters was studied in the three-stage purification of aluminate solution from the Bayer process and aluminum hydroxide. One of the ways of achieving this kind of purification is treating the aluminate solution in order to reduce the concentrations of the starting raw material (solution) and then treating the aluminum hydroxide at a certain temperature and for a given time in order to obtain an alumina precursor of adequate quality. The purification process itself is divided into three phases. The first phase involves the treatment of sodium aluminate with lime, primarily in order to remove Ca^{2+} and $(SiO_3)^{2-}$ impurities. Phase II aims to remove the impurities of Zn^{2+}, Fe^{2+}, and Cu^{2+} by treatment with controlled precipitation using specially prepared crystallization centers. In Phase III, Na^+ is removed by the process of the hydrothermal washing of $Al_2O_3{\cdot}3H_2O$. In this work, parameters such as temperature (T), reaction time (t), and concentration of lime (c) were studied in order to remove the mentioned impurities and obtain the purest possible product that would be an adequate precursor for special types of alumina.

5. Electrochemical methods for metal refining and winning (Recovery of Rare Earth Elements from Spent NdFeB Magnets: Metal Extraction by Molten-Salt Electrolysis (Part III)). The results obtained from work on the concept of a recycling process for NdFeB magnets that seeks to recover rare earth elements for the remanufacturing similar magnets are presented aiming at the winning of the metals. This paper investigates the viability of extracting rare earth metals from magnet recycling-derived oxide (MRDO) by means of molten salt electrolysis. The MRDO was produced from spent NdFeB magnets through oxidation in air and subsequently carbothermic reduction under an 80 mbar Ar gas atmosphere. This MRDO contained roughly 33 wt.% Nd and 10 wt.% Pr. The electrochemical reduction process of the MRDO on molybdenum electrodes in NdF_3 + LiF and NdF_3 + PrF_3 + LiF fused-salt systems was investigated by cyclic voltammetry and chronoamperometry measurements. The resulting electrolytes and electrodes were examined after potentiostatic deposition by scanning electron microscopy (SEM), inductively coupled plasma optical emission spectroscopy (ICP-OES), and X-ray diffraction (XRD) analysis. The electrodeposited metals appeared to accumulate on the cathode and X-ray diffraction analysis confirmed the formation of metallic Nd and Pr on the working substrate. The suitability of the obtained alloy, intended for the remanufacturing of NdFeB magnets, was then evaluated.
6. Synthesis of metallic, oxidic, and composite methods using different processes (1. Synthesis of Complex Concentrated Nanoparticles by Ultrasonic Spray Pyrolysis and Lyophilization; and 2. Transformation of Iron (III) Nitrate from an Aerosol by Ultra-

sonic Spray Pyrolysis and Hydrogen Reduction). Following the leaching of different materials, the purification of a solution, and filtration, the winning of metals from the cleaned solution is the next required step. Simic et al. studied the development of new multicomponent nanoparticles, which are gaining increasing importance due to their specific functional properties, i.e., new complex concentrated nanoparticles (CCNPs) synthesized in the form of a powder using ultrasonic spray pyrolysis (USP) and lyophilization from the initially cast $Ag_{20}Pd_{20}Pt_{20}Cu_{20}Ni_{20}$ alloy, which was in the function of the material after its catalytic abilities had been exhausted. Hydrometallurgical treatment was used to dissolve the cast alloy, from which the USP precursor was prepared. As a consequence of the incomplete dissolution of the cast alloy and the formation of Pt and Ni complexes, it was found that the complete recycling of the alloy was not possible. A microstructural examination of the synthesized CCNPs showed that round and mostly spherical (not 100%) nanoparticles with an average diameter of 200 nm were formed. The study shows that CCNPs belong to a group with medium entropy characteristics. A mechanism for the formation of CCNPs is proposed, based on the thermochemical analysis of element reduction with the help of H_2, and also based on the mixing enthalpy of binary systems Due to their unique properties, iron nanoparticles find diverse applications across various fields, including catalysis, electronics, wastewater treatment, and energy storage. These particles are mostly sub-micrometer in size and are highly reactive to both air (oxygen) and water, and, in nanoparticles (with a size below 100 nm), this process is even more rapid than for the bulk material. This characteristic limits the use of these nanoparticles to inert environments. Iron nanoparticles are not toxic and are mostly used for wastewater treatment. Understanding the hydrogen reduction mechanisms and conditions that lead to the formation of metallic iron particles from iron (III)-nitrate from an aerosol is crucial in terms of enabling their effective utilization, as shown in Figure 1. This research studied the hydrogen reduction behavior of Fe_2O_3 in the absence and presence of additives (SiO_2 or Pt) via ultrasonic spray pyrolysis.

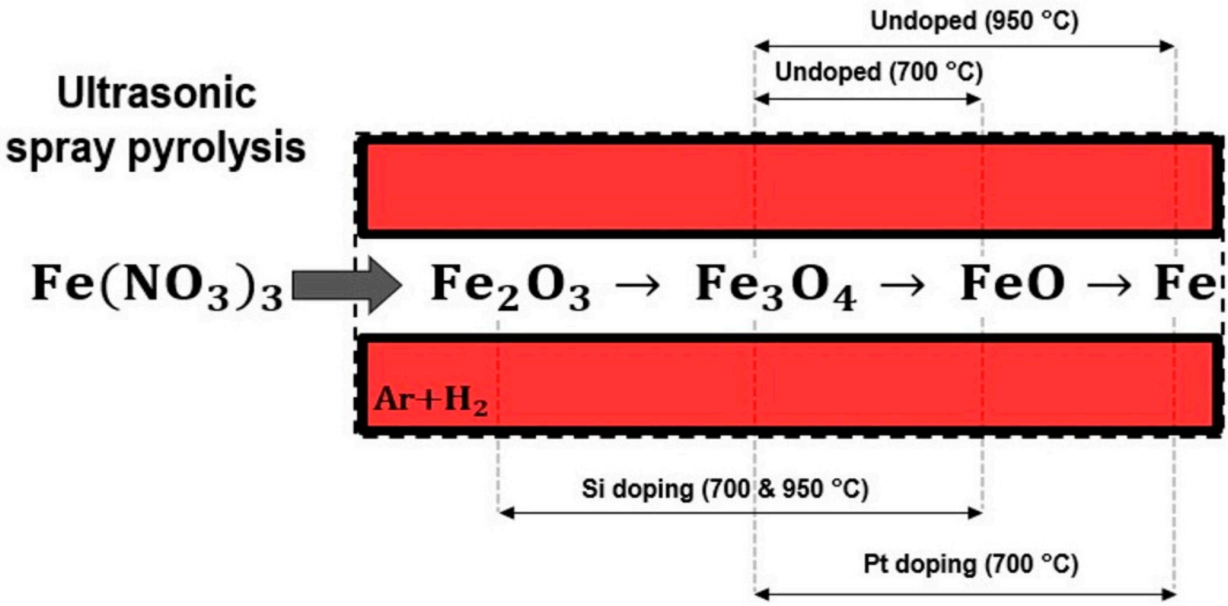

Figure 1. Formation of iron particles in the presence of platinum and SiO_2.

The characterization was performed with a scanning electron microscope, energy-dispersive X-ray spectroscopy, and X-ray diffraction. In the absence of additives, the oxygen content of iron oxide particles decreased with increasing temperature from 700 to 950 °C but significantly increased with the doping of 10 mL (40 wt.%) of SiO_2. The inhibitory effect of Si on the hydrogen reduction of the Fe_2O_3 formed was more pronounced at 950 °C than at 700 °C. In contrast, the doping of only 5 mL (15 wt.%) of Pt significantly decreased the oxygen concentration in the synthesized particles by catalyzing the reduction reaction of iron oxides at 700 °C. The metallic iron (Fe) product, obtained in the undoped iron oxides run at only 950 °C, was also formed at 700 °C in the Pt-doped Fe_2O_3 run.

Binnemans and Jones [6] proposed the 12 principles of a novel and more sustainable approach to hydrometallurgy that they call "circular hydrometallurgy". This paper can form the basis of the future identification of areas of research in the field of the unit operations of hydrometallurgy, while providing a "sustainability" benchmark for assessing existing processes and technological developments, aiming at the design of energy-efficient and resource-efficient flowsheets or unit processes that consume the minimum quantities of reagents and result in minimum waste.

3. Conclusions

Advances in the understanding of unit operations in non-ferrous extractive metallurgy are focused on six different subjects: roasting; smelting; leaching; purification of solutions during anodic oxidation, precipitation and neutralization; molten salt electrolysis; and the synthesis of powders using ultrasonic spray pyrolysis with hydrogen reductions and lyophilization (totally 28 papers). The leaching process was presented using primary materials such as nickel lateritic ores and pyrolyzed printed circuit boards, confirming the importance of the influence of reaction parameters. This paper proposes a pyrometallurgical recycling method for end-of-life NdFeB magnets by pyrometallurgical treatment composed by oxidation in air, carbothermic reduction, and molten-salt electrolysis. The future applications of the unit operations in non-ferrous extractive metallurgy will be deeply connected with circular hydrometallurgy, digitalization, and artificial neural networks.

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References

1. Božinović, K.; Štrbac, N.; Mitovski, A.; Sokić, M.; Minić, D.; Marković, B.; Stojanović, J. Thermal Decomposition and Kinetics of Pentlandite-Bearing Ore Oxidation in the Air Atmosphere. *Metals* **2021**, *11*, 1364. [CrossRef]
2. Drobe, M.; Haubrich, F.; Gajardo, M.; Marbler, H. Processing Tests, Adjusted Cost Models and the Economies of Reprocessing Copper Mine Tailings in Chile. *Metals* **2021**, *11*, 103. [CrossRef]
3. Marjanović, V.; Perić-Grujić, A.; Ristić, M.; Marinković, A.; Marković, R.; Onjia, A.; Šljivić-Ivanović, M. Selenate Adsorption from Water Using the Hydrous Iron Oxide-Impregnated Hybrid Polymer. *Metals* **2020**, *10*, 1630. [CrossRef]
4. Rudolf, R.; Stambolic, A.; Kocijan, A. Atomic Layer Deposition of a TiO_2 Layer on Nitinol and Its Corrosion Resistance in a Simulated Body Fluid. *Metals* **2021**, *11*, 659. [CrossRef]
5. Liakyn, L.; Onalbayeva, Z.; Kulenova, K.; Daumova, G.; Mamyachenkov, S. Anisimova, Research of the Process of Purification of Sulfate Zinc Solution from Iron Ions Using Anodic Oxidation. *Metals* **2023**, *13*, 88. [CrossRef]
6. Binnemans, K.; Jones, T. The Twelve Principles of Circular Hydrometallurgy. *J. Sustain. Metall.* **2023**, *9*, 1–25. [CrossRef]