

## Article

# Modeling the Leaching of Cobalt and Manganese from Submarine Ferromanganese Crusts by Adding Steel Scrap Using Design of Experiments and Response Surface Methodology

Kevin Pérez <sup>1</sup>, Norman Toro <sup>2,\*</sup> , Mauricio Mura <sup>2</sup>, Manuel Saldana <sup>2</sup> , Felipe M. Galleguillos Madrid <sup>3</sup> , Iván Salazar <sup>4</sup>, Francisco Javier González <sup>5</sup> , Egidio Marino <sup>5</sup> , Jonathan Castillo <sup>6</sup> , Ignacio Castillo <sup>2</sup> and Pía C. Hernández <sup>1,7,\*</sup> 

- <sup>1</sup> Departamento de Ingeniería Química y Procesos de Minerales, Facultad de Ingeniería, Universidad de Antofagasta, Antofagasta 1240000, Chile; kevin.perez@sqm.com
  - <sup>2</sup> Faculty of Engineering and Architecture, Universidad Arturo Prat, Iquique 1110939, Chile; mauricio.mura@alumnos.ucn.cl (M.M.); masaldana@unap.cl (M.S.); icp005@alumnos.ucn.cl (I.C.)
  - <sup>3</sup> Centro de Desarrollo Energético Antofagasta, Universidad de Antofagasta, Antofagasta 1240000, Chile; felipe.galleguillos.madrid@uantof.cl
  - <sup>4</sup> Departamento de Ingeniería Civil, Universidad Católica del Norte, Antofagasta 1270709, Chile; isalazar@ucn.cl
  - <sup>5</sup> Instituto Geológico y Minero de España (IGME-CSIC), Ríos Rosas, 23, 28003 Madrid, Spain; fj.gonzalez@igme.es (F.J.G.); e.marino@igme.es (E.M.)
  - <sup>6</sup> Departamento de Ingeniería en Metalurgia, Universidad de Atacama, Copiapó 1531772, Chile; jonathan.castillo@uda.cl
  - <sup>7</sup> Centro de Economía Circular en Procesos Industriales (CECPI), Facultad de Ingeniería, Universidad de Antofagasta, Av. Angamos 601, Antofagasta 1270300, Chile
- \* Correspondence: notoro@unap.cl (N.T.); pia.hernandez@uantof.cl (P.C.H.); Tel.: +56-975-387-250 (N.T.)



Academic Editor: Nikolaos Koukouzas

Received: 17 December 2024

Revised: 15 January 2025

Accepted: 20 January 2025

Published: 23 January 2025

**Citation:** Pérez, K.; Toro, N.; Mura, M.; Saldana, M.; Madrid, F.M.G.; Salazar, I.; González, F.J.; Marino, E.; Castillo, J.; Castillo, I.; et al. Modeling the Leaching of Cobalt and Manganese from Submarine Ferromanganese Crusts by Adding Steel Scrap Using Design of Experiments and Response Surface Methodology. *Appl. Sci.* **2025**, *15*, 1155. <https://doi.org/10.3390/app15031155>

**Copyright:** © 2025 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/>).

**Abstract:** Due to the scarcity of high-grade minerals on the Earth's surface and the ever-increasing demand for critical metals required in the production of clean energy, the search for alternative sources has become essential. Ferromanganese crusts, a mineral resource located in the depths of the ocean, contain high concentrations of valuable metals, particularly cobalt (Co) and manganese (Mn). A leaching process using sulfuric acid, with the addition of steel scrap, has been proposed for processing this resource. The study investigated the extraction of manganese (Mn) and cobalt (Co) under acidic conditions at 25 °C, employing a factorial experimental analysis. Statistical models were adjusted using response surface methodology to evaluate the effects of time and the ferromanganese crust/Fe(res) (iron residue) ratio as predictive variables. The results demonstrated that the extraction of Mn and Co could be effectively modeled through multiple regression, with strong goodness-of-fit indicators. Optimal extraction was achieved at extended durations (30 min) and lower ferromanganese crust/Fe(res) ratios (1/3) for the sampled values. Gradient analysis revealed that extraction efficiency was directly proportional to time and inversely proportional to the ferromanganese crust/Fe(res) ratio, except in the case of Co extraction at higher durations and lower ratio levels. Additionally, no precipitation of Mn or Co species was observed in the analyzed residues.

**Keywords:** leaching; deep-sea mining; optimization; crusts

## 1. Introduction

The increasing demand for critical raw materials, driven by their essential role in clean energy technologies, has raised concerns about potential supply shortages. Developing countries, particularly in Africa, which possess 30% of the world's mineral reserves, are

pivotal sources of these materials [1,2]. Critical minerals such as cobalt (Co), lithium (Li), nickel (Ni), and manganese (Mn) are essential to produce clean energy technologies [3–5]. The demand for these minerals is particularly significant in the production of electric vehicle batteries, with each battery requiring up to 200 kg of essential minerals. Notably, the battery sector accounts for 70% of the global demand for cobalt [6–8]. For this reason, these minerals are classified as ‘critical raw materials’ due to their immense importance and the limited availability of reserves on the Earth’s surface [9]. Consequently, a steady increase in their demand is expected in the medium to long term (see Figure 1).

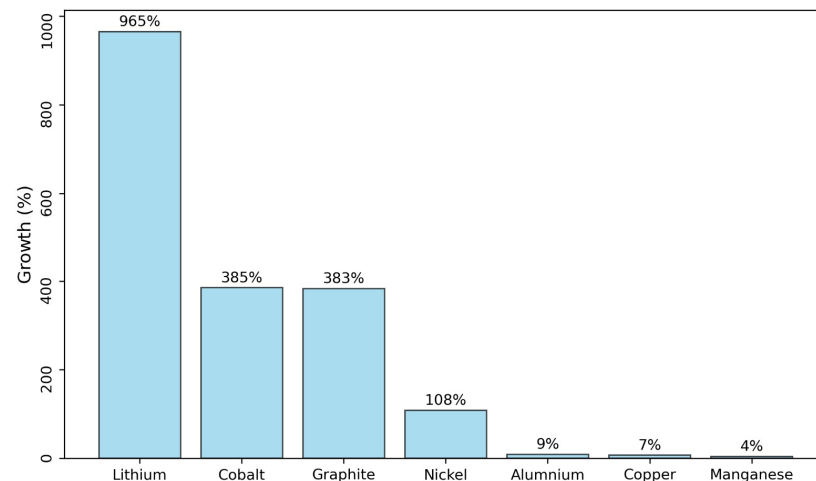


**Figure 1.** Projection of the value of critical metals for the year 2050 (modified from Toro et al. [1]).

It is imperative to generate fresh momentum to address the stagnation in the growth capacity of the terrestrial mining industry. Large-scale mining, which plays a critical role in surplus production, faces significant challenges, chief among them being the decline in ore grades. To compensate for this deterioration and maintain profitability, overexploitation becomes prevalent, leading to the substantial generation of polluting waste, such as tailings [7,10–13].

Among the minerals found on the seafloor, ferromanganese crusts offer a promising alternative for the recovery of metals required in contemporary clean technologies, particularly due to their high Co and Mn content [14–16]. These resources are distributed across the global oceanic expanse, occurring at depths ranging from 400 to 7000 m along the slopes of submarine mountains and ridges [17], and plateaus. There are few studies on the co-processing of ferromanganese crusts for Co and Mn extraction, a process that generally involves leaching with a reducing agent and, in some cases, preliminary roasting steps.

With respect to studies that specifically utilize steel slag as a reducing agent and sulfuric acid to recover Co and Mn from underwater mineral resources, two recent investigations stand out. In the study by Pérez et al. [12], it was demonstrated that Co and Mn could be jointly dissolved from marine nodules, with the best results achieved using a reducing agent ratio of 1:2 (nodule/steel slag) at 60 °C for a duration of 15 min. This process resulted in extraction efficiencies of 98% for Mn and 55% for Co. Subsequently, Pérez et al. [12] replicated these conditions to recover Co and Mn from ferromanganese crusts. The researchers found that the optimal results were obtained with a reducing agent ratio of 1:2 (Fe-Mn crust/steel slag) at 60 °C for 10 min, achieving joint extraction efficiencies of approximately 80% for Co and ~40% for Mn. The proposed reactions (Reactions (1)–(4)) for the dissolution of Co and Mn from ferromanganese crusts using foundry slags and H<sub>2</sub>SO<sub>4</sub> are outlined in Table 1.

**Table 1.** Suggested reactions for the extraction of Co and Mn from deep-sea minerals [12].

| Reaction                                                                                                                                                                                                       | $\Delta G^\circ$ (kJ) | Reaction No. |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------|--------------|
| $\text{Fe}_3\text{O}_4 (\text{s}) + 4\text{H}_2\text{SO}_4 (\text{l}) \leftrightarrow \text{FeSO}_4 (\text{aq}) + \text{Fe}_2(\text{SO}_4)_3 (\text{s}) + 4\text{H}_2\text{O} (\text{l})$                      | −264.27               | (1)          |
| $2\text{FeSO}_4 (\text{aq}) + 2\text{H}_2\text{SO}_4 (\text{aq}) + \text{MnO}_2 (\text{s}) \leftrightarrow \text{Fe}_2(\text{SO}_4)_3 (\text{s}) + 2\text{H}_2\text{O} (\text{l}) + \text{MnSO}_4 (\text{aq})$ | −221.44               | (2)          |
| $\text{CoO} + \text{H}_2\text{SO}_4 \leftrightarrow \text{CoSO}_4 + \text{H}_2\text{O}$                                                                                                                        | −115.43               | (3)          |
| $\text{Co}_3\text{O}_4 + 4\text{H}_2\text{SO}_4 + 2\text{FeSO}_4 \leftrightarrow 3\text{CoSO}_4 + 4\text{H}_2\text{O} + \text{Fe}_2(\text{SO}_4)_3$                                                            | −354.18               | (4)          |

In this study, a novel acid-reductive leaching mechanism is proposed, repurposing steel residue (slag) from the Chilean steel industry for the joint recovery of Co and Mn from ferromanganese crusts. This approach offers a sustainable solution to resource recovery, minimizing waste and the environmental impact associated with traditional mining methods. The response surface methodology (RSM) and design of experiments (DOE) were employed to optimize the leaching parameters, ensuring maximum recovery efficiency and showcasing the potential for industrial applications within circular economic practices. The utilization of RSM and DOE to model the leaching parameters for Co and Mn is pivotal in optimizing and understanding the complex interactions between various process variables in laboratory experiments. These methodologies provide a structured framework for DOE, enabling the efficient exploration of the effects of multiple factors and their interactions on leaching outcomes. This is particularly advantageous in leaching processes, where variables such as pH, temperature, reagent concentration, and time significantly influence the extraction efficiency of metals like Co and Mn. RSM has proven effective in optimizing leaching conditions by evaluating the impact of multiple variables and their interactions. For instance, in the study of Co dissolution, RSM facilitated the identification of optimal conditions for Co recovery, achieving an impressive recovery rate of 95.79% under specific conditions of pH, temperature, and ferrous sulphate concentration [18]. Similarly, RSM has been utilized to optimize Mn leaching from low-grade ores by identifying the critical interaction between  $\text{H}_2\text{SO}_4$  concentration and the quantity of glucose [19]. Complementarily, DOE provides a systematic and efficient approach to exploring the experimental space, minimizing the number of experiments needed to comprehend the system. This is exemplified using central composite design within RSM, which effectively examines the influence of variables on leaching outcomes. Notably, both RSM and DOE excel in modeling complex interactions between variables, a critical feature in leaching processes where multiple factors may interact in a non-linear manner. For instance, the interaction between leaching time and the quantity of ferrous sulphate has been identified as significant in cobalt dissolution [18].

Recent studies have investigated optimization techniques for Cu and Co extraction from ores, emphasizing the use of RSM and DOE. Response surface methodology (RSM) and artificial neural networks (ANN) have been applied to model and predict leaching behavior [20,21]. RSM has been used to optimize parameters such as particle size, temperature, and redox potential for Cu extraction from chalcopyrite [22,23]. Similarly, RSM has been applied to optimize leaching parameters for Cu extraction from hematite-dominated ore, considering acid concentration, temperature, and contact time [24]. ANN models have shown high accuracy in predicting copper and cobalt recovery, with correlation coefficients exceeding 0.95 [20,21]. DOE approaches, such as central composite design, have been employed to investigate and optimize operational conditions for Cu ion recovery using emulsion liquid membrane methods [25]. These modeling techniques provide valuable tools for enhancing extraction processes and underscore the effectiveness of employing and/or combining RSM, DOE, and ANN methods for optimizing and predicting outcomes in the hydrometallurgical extraction of copper and cobalt. This approach offers improved efficiency and higher recovery rates. Finally, understanding the impact of time and the

crust/Fe ratio on the leaching process of Co and Mn from ferromanganese submarine crusts is crucial to optimizing efficiency, reducing costs, and improving process sustainability. Analyzing leaching time helps determine the duration required to achieve maximum dissolution of the target metals. Insufficient time may result in incomplete recovery, while excessive durations can lead to inefficiencies and increased costs. The crust/Fe ratio, on the other hand, ensures an adequate amount of leaching agent is available to dissolve the metals without wasting chemical reagents. Striking a balance between the quantity of mineral and the leaching agent minimizes excessive reagent use, significantly reducing operating costs while avoiding issues such as solution saturation or the formation of unwanted precipitates.

Examining the relationship between these parameters allows for the fine-tuning of operating conditions to maintain consistent and predictable extraction, reducing variability and enhancing process stability. In summary, a detailed analysis of these variables not only improves the technical and economic efficiency of the leaching process but also delivers operational and environmental benefits essential for modern, sustainable operations.

## 2. Background

These modeling techniques provide valuable tools for enhancing extraction processes and underscore the effectiveness of employing and/or combining RSM, DOE, and ANN methods for optimizing and predicting outcomes in the hydrometallurgical extraction of Cu and Co. This approach offers improved efficiency and higher recovery rates. Finally, understanding the impact of time and the crust/Fe ratio on the leaching process of Co and Mn from ferromanganese submarine crusts is crucial to optimizing efficiency, reducing costs, and improving process sustainability. Analyzing leaching time helps determine the duration required to achieve maximum dissolution of the target metals. Insufficient time may result in incomplete recovery, while excessive durations can lead to inefficiencies and increased costs. The crust/Fe ratio, on the other hand, ensures an adequate amount of leaching agent is available to dissolve the metals without wasting chemical reagents. Striking a balance between the quantity of mineral and the leaching agent minimizes excessive reagent use, significantly reducing operating costs while avoiding issues such as solution saturation or the formation of unwanted precipitates. Examining the relationship between these parameters allows for the fine-tuning of operating conditions to maintain consistent and predictable extraction, reducing variability and enhancing process stability. In summary, a detailed analysis of these variables not only improves the technical and economic efficiency of the leaching process but also delivers operational and environmental benefits essential for modern, sustainable operations [26,27]. Methods such as population balance modeling (PBM) are employed to predict the distribution of particle sizes in processes like grinding and flotation, supporting the design and optimization of these operations [26].

In terms of the contribution of modeling to mineral processing, models such as the MiSCOR model for the upstream supply chain play a significant role. This model addresses the dynamics of the upstream segment of the mineral supply chain, offering a standardized framework that seamlessly integrates with the downstream segment. It is specifically designed to enhance collaboration and decision-making in mineral supply chain management [28]. Another noteworthy model is model predictive static programming (MPSP), a technique applied to control problems in mineral processing, such as grinding and flotation circuits. MPSP provides computational efficiency and enhanced performance compared to traditional methods, making it a highly viable option for achieving optimal control in mineral processing plants [29].

Geochemical modeling for mineralization processes is another approach with extensive applications in mineral processing management. This method is vital for developing mineralization processes, particularly in the context of CO<sub>2</sub> utilization. It supports feedstock selection and process engineering by predicting product speciation in complex systems [30]. Mathematical modeling of particle motion is utilized to simulate particle movement in enrichment devices, aiding in the identification of effective parameters for optimizing the enrichment process [31]. Process simulations are employed to model mineral processing operations at various levels, ranging from bulk processes to mineral-specific models. These simulations provide valuable insights into the processing of Fe ore and other minerals, aiding in their optimization and improved efficiency [32]. Algorithms and simulation models are developed to optimize the transport and unloading of mineral resources, enhancing operational efficiency and reducing costs [33]. While the primary focus of mineral process modeling is on enhancing efficiency and sustainability, challenges such as integrating various modeling techniques and the need for standardized frameworks persist. The adoption of artificial intelligence and advanced computational methods is continually evolving, presenting new opportunities for innovation in mineral processing. However, the complex nature and inherent variability of mineral processing systems demand ongoing research and development efforts to fully realize the potential of these modeling methodologies. The extraction of Cu and Co is a complex process that requires the application of various modeling methods to optimize efficiency and yield. These methodologies are crucial for addressing the challenges posed by the unique chemical properties of copper and cobalt ores, as well as the diverse mineralogical composition of the feed material. The sections below explore different modeling approaches and techniques employed in the extraction of these metals.

- **Redox Chemistry in Ore Processing:** A dual-benefit strategy harnesses the redox properties of Cu and Co ores, enabling simultaneous extraction without the need for additional oxidizing or reducing agents. This approach achieves high recovery efficiencies of 99.67% for copper and 98.20% for cobalt by capitalizing on the oxidizing properties of Co<sup>3+</sup> in oxide ores and the reducibility of sulfide ores [34].
- **Neural Networks and Response Surface Methodology:** This approach has been implemented to forecast and improve the leaching characteristics of Cu-Co ores. The ANN employs a backpropagation algorithm to model the process, while RSM utilizes the Box-Behnken design for optimization. The method achieves leaching yields of 93.46% for Cu and 89.43% for Co, with a strong correlation between predicted and experimental values [20].
- **Ammonium Sulfate Roasting:** An innovative method involves ammonium sulphate roasting for the selective extraction of metals from oceanic Co-rich crusts. This process converts metal oxides into sulphates, achieving high leaching efficiencies for Co, Ni, and Cu, while minimizing Fe leaching. The method is efficient, environmentally friendly, and economically advantageous compared to traditional techniques [35,36].
- **Metal Melt Extraction:** A method involving metal melting entails heating a Cu-Co alloy with a metal extraction medium under an inert atmosphere, effectively separating Cu from the alloy. The extracted Cu can then be utilized as a high-quality raw material, while the remaining alloy is suitable for further processing, such as acid leaching [37].
- **Pressure Leaching and Electrodeposition:** The extraction of cathode Cu from Co concentrate involves pressure leaching, followed by Cu recovery and electrodeposition. This process incorporates steps for the removal and recycling of extractants, improving the efficiency of the extraction process and enhancing the quality of the final Cu product [38,39].

- **Continuous Fluid Separation:** A production method for extracting Co from Cu extraction tail liquid utilizes a continuous fluid separation system with chelate resin. This approach streamlines the process, reduces costs, and enhances cobalt purification efficiency by eliminating the need for traditional precipitation steps [40].
- **Taguchi Method and ANOVA:** The Taguchi method and analysis of variance (ANOVA) are employed to optimize heap leaching conditions for Cu and Co recovery from tailings. This statistical approach identifies optimal leaching parameters, including particle size, acidity, and flow rate, leading to significant metal recovery rates [41].
- **Microfluidic Extraction:** A procedure is employed to separate Cu and Co ions in a microchannel by optimizing parameters such as pH, flow rate, and extractant concentration. This method achieves a high Cu extraction rate while minimizing Co co-extraction, providing a more efficient and effective separation process [42].

The formulation of extraction processes for Cu and Co through the application of response surface methodology (RSM) and design of experiments (DOE) necessitates the optimization of numerous process parameters to enhance the efficiency and yield of extraction methods. RSM is a statistical approach used for modeling and analyzing problems where multiple variables influence the response of interest, with the goal of optimizing this response. DOE, on the other hand, is a structured methodology designed to elucidate the relationship between factors affecting a process and the resulting output. Together, these methodologies provide a robust framework for optimizing extraction processes. The optimization of process parameters using RSM in the extraction of copper and cobalt has proven highly effective in refining key variables. For instance, during the extraction of Cu from sulfuric solutions containing cobalt, RSM was utilized to fine-tune parameters such as the initial pH, volumetric flow rate, and extractant concentration. This approach achieved a Cu extraction efficiency of 96.73%, while simultaneously minimizing Co extraction to just 2.41% [42]. Similarly, RSM was employed to optimize the leaching conditions for cobalt dissolution from heterogenite, identifying critical factors such as the ferrous sulphate dosage, leaching time, and temperature [18]. Methodologies such as the Box-Behnken design and central composite design (CCD) have been utilized to analyze the effects of various factors on extraction processes. For example, the Box-Behnken design was used to model the leaching behavior of Cu-Co ores, considering parameters such as solid percentage, time, particle size, and  $\text{Fe}^{2+}$  ion concentration [20]. CCD was employed to evaluate cobalt ion extraction using an aqueous two-phase system, highlighting the influence of cobalt ion concentration and volume on extraction efficiency [43].

The integration of response surface methodology (RSM) with artificial neural networks (ANN) has been investigated to enhance prediction accuracy and process optimization. In one study, ANN was combined with RSM to model the leaching behavior of Cu-Co ores, achieving high correlation coefficients and low root mean square errors, highlighting the effectiveness of this integrated approach [20]. RSM has also been employed in the design of counter-current leaching systems for Cu extraction, optimizing factors such as acid consumption, iron concentration, and leaching time. This approach improved overall leaching efficiency by up to 80% [44]. The application of RSM in developing environmentally sustainable extraction techniques, such as aqueous two-phase systems, demonstrates its potential to reduce the environmental impact associated with traditional extraction methods. This approach replaces hazardous organic solvents with water, aligning with sustainable and eco-friendly practices [43]. The optimized extraction processes developed through RSM and DOE have significant industrial applications, particularly in the recovery of metals from low-grade ores and waste materials.

While RSM and DOE are powerful tools for optimizing extraction processes, their integration with advanced modeling techniques, such as artificial neural networks (ANNs),

can significantly enhance the robustness and applicability of these models across diverse industrial settings. Moreover, the shift towards eco-friendly extraction methods highlights the crucial importance of sustainable practices within the field of metallurgy.

Although considerable progress has been made in the extraction of Cu and Co, challenges remain, including the variability in ore mineralogy and the pressing need for sustainable methodologies. Future research efforts could focus on combining these approaches with emerging technologies to further improve efficiency and promote environmental sustainability. In the context of Co leaching, RSM has been employed to model the effects of various parameters, such as acid concentration and the presence of a reducing agent, offering valuable insights into the optimal conditions for maximizing Co recovery [45]. The use of mathematical models and simulations further aids in understanding the dynamic behavior of the leaching process. For Mn, RSM has been applied to optimize the reductive leaching process, exploring various reducing agents and acid concentrations. This methodology identifies the most significant variables influencing Mn extraction, enabling the achievement of high extraction efficiencies [19,46].

### 3. Materials and Methods

#### 3.1. Ferromanganese Crusts

Studied samples were recovered in the course of two different cruises performed by the Geological Survey of Spain (IGME): sample DRAGO 0511/DR04-15 was sampled during the DRAGO 0511 cruise on board the *RV Miguel Oliver* on the Echo Seamount, located 263 nautical miles southwest of Canary Islands; while sample SUBVENT 1/DA06-4 was recovered through the SUBVENT 1 cruise on board *RV Hespérides* on the Gaire Seamount, sited 240 nautical miles west-southwest to Canary Islands (see Figure 2).

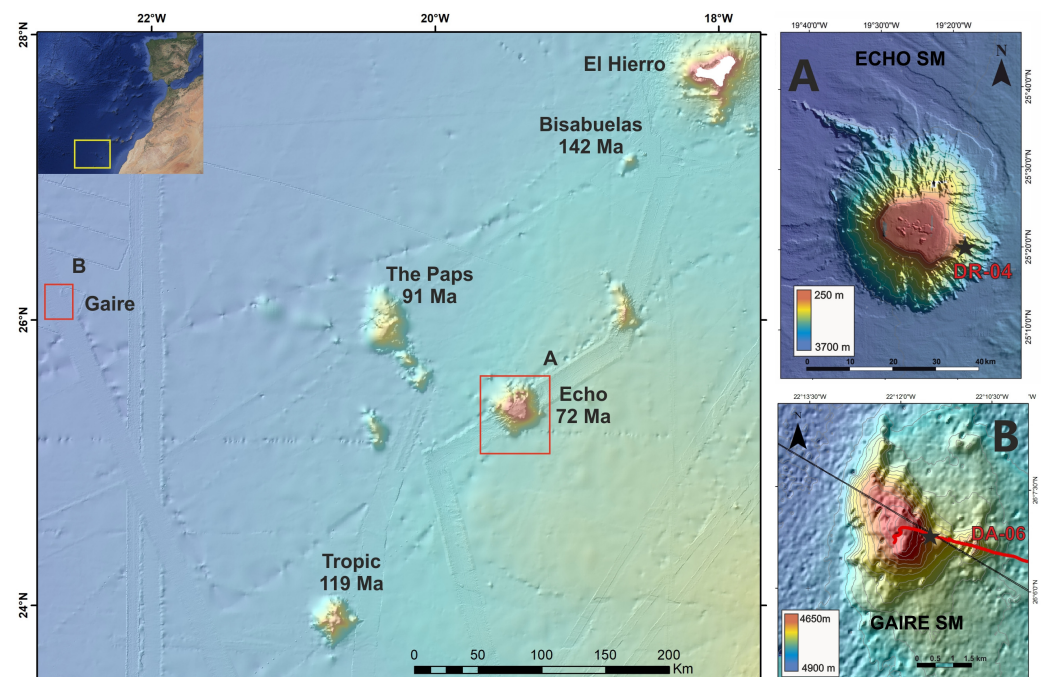


**Figure 2.** Canary Islands Seamounts Province (CISP) regional setting. Bathymetric view of the study area on the left and zoom of the studied seamounts and sampling sites on the right, ages from van den Bogaard [47], and Somoza [48] (Echo age).

Both seamounts are part of the Canary Islands Seamount Province, which forms an ancient seamount track in the north-east Atlantic Ocean, dating back to the Cretaceous period (approximately 142–72 Ma). Co-rich ferromanganese deposits are found covering

these seamounts as almost continuous pavements with varying thicknesses (0.1–25 cm). The Echo Seamount is a guyot-type seamount (Figure 2A), characterized by a conical structure with a flat summit, rising from 3700 m to 250 m at its peak. The sample studied, recovered via dredging on the eastern flank, exhibited an average thickness of 2.5 cm. In contrast, Gaire Seamount is a very deep and small structure with a ridge-like morphology-oriented NNW–SSE. It measures 6 km in length and 5 km in width in the region of its secondary cone, at depths ranging from 4900 to 4650 m (Figure 2B). The studied sample was also recovered via dredging along a track from ESE to WNW and displayed a thickness of 6.4 cm.

### 3.2. Iron Residue

The steel residue, or “slag”, was sourced from the steel smelting operations of CAP Company in Chile. This by-product comprised 82.65%  $\text{Fe}_3\text{O}_4$ , 13.03%  $\text{Fe}_2\text{O}_3$ , and 0.27% metallic iron (see Table 2). Initially, the slag particles ranged in size from 1 to 10 mm; however, they were subsequently ground using a mortar to reduce their size, producing particles within the range of  $-140$  to  $+100\ \mu\text{m}$ .

**Table 2.** Chemical analysis of steel residue.

| Element                 | Mass (wt. %) |
|-------------------------|--------------|
| $\text{Fe}_3\text{O}_4$ | 82.65        |
| $\text{Fe}_2\text{O}_3$ | 13.03        |
| $\text{Fe}^0$           | 0.27         |
| CaO                     | 0.75         |
| $\text{SiO}_2$          | 1.5          |
| $\text{Al}_2\text{O}_3$ | 0.3          |
| MgO                     | 0.2          |
| $\text{SO}_3$           | 0.08         |
| $\text{P}_2\text{O}_5$  | 0.2          |
| $\text{K}_2\text{O}$    | 0.015        |
| MnO                     | 0.8          |
| C                       | 0.2          |

### 3.3. Leaching Test

Leaching tests were conducted in a 200 mL glass reactor with a solid-to-liquid ratio of 0.1 (100 mL of acid solution). A total of 10 g of ferromanganese crusts was maintained in suspension and agitated using a 5-position magnetic stirrer (IKA ROS, CEP 13087-534, Campinas, Brazil) at 600 rpm, with a particle size range of  $-140$  to  $+100\ \mu\text{m}$ . The temperature was controlled using an oil-heated circulator (Julabo, St. Louis, MO, USA), and experiments were conducted at temperatures ranging from 25 to 60 °C. All tests were performed in duplicate, with analysis carried out using 5 mL undiluted samples analyzed via atomic absorption spectroscopy (AAS), ensuring a variation quotient of  $\leq 5\%$  and a relative difference of 5–10%. The pH and oxidation-reduction potential (ORP) of the leaching solutions were measured using a pH-ORP meter (HANNA HI-4222, St. Louis, MO, USA). ORP measurements were taken with a platinum electrode cell and a saturated Ag/AgCl reference electrode.

### 3.4. Estimation of Factorial DOE

To address this and investigate Mn and Co extraction from ferromanganese crusts, two independent variables were selected for a factorial design comprising 32 experiments: time and the ferromanganese crust/Fe(res) ratio. The experiments were conducted under controlled conditions to evaluate the influence of these variables on extraction efficiency.

The results demonstrated a significant correlation between extraction efficiency and both variables, identifying optimal conditions for maximizing Mn and Co recovery. This methodology enables the evaluation of the most significant variables and their respective impacts while providing an experimental framework that, through coefficient calculation, facilitates the optimization of the response variable [49–51]. A factorial design was applied involving two factors, each one having three levels; thus, 9 experimental tests were carried out, obtaining the response variables Mn and Co extraction. Minitab 18 software was used for the experimental design and development of a multiple regression equation [52].

Then, the explained variable was expressed based on linear effect of explanatory variables and considering the effects of interaction and curvature, as shown in Equation (1).

$$Mn|Co \text{ Extraction } (\%) = \alpha + \sum_{\forall i} \beta_i x_i + \sum_{\forall i} \sum_{\forall j} \beta_{ij} x_i x_j, \forall i, j \in \{time, crust/Fe\} \quad (1)$$

where  $\alpha$  is an overall constant,  $x_i$  is the value of the level  $i$  of the factor  $x$ ,  $\beta_i$  is the coefficient of the linear factor  $x_i$ ,  $\beta_{ij}$  is the coefficient of the interactions  $x_i \cdot x_j$ , and Mn and Co extraction are the dependent variables.

Table 3 shows the values of the levels for each factor, while Table 4 shows the recovery obtained for each configuration.

**Table 3.** Experimental conditions.

| Parameters [Variable]/Values           | Low | Medium | High |
|----------------------------------------|-----|--------|------|
| Time (min) [ $x_1$ ]                   | 10  | 20     | 30   |
| Ferromanganese Crust/Fe(res) [ $x_2$ ] | 1/3 | 1/2    | 1/1  |
| Codifications                          | −1  | 0      | 1    |

**Table 4.** Experimental configuration and Cu and Co extraction.

| Sample |            | Drago 0511/DR04-15 [S1]      |                   |                   | Subvent 1/DA06-4 [S2] |                   |
|--------|------------|------------------------------|-------------------|-------------------|-----------------------|-------------------|
| Test   | Time (min) | Ferromanganese Crust/Fe(res) | Mn Extraction (%) | Co Extraction (%) | Mn Extraction (%)     | Co Extraction (%) |
| 1      | −1         | −1                           | 74.15             | 31                | 73.95                 | 29                |
| 2      | −1         | 0                            | 69.5              | 28                | 71.25                 | 27.5              |
| 3      | −1         | 1                            | 55                | 20.55             | 56.5                  | 17.6              |
| 4      | 0          | −1                           | 72.45             | 32.8              | 73.45                 | 31                |
| 5      | 0          | 0                            | 74.21             | 31.5              | 74.21                 | 30                |
| 6      | 0          | 1                            | 67.8              | 27.25             | 66.7                  | 26.55             |
| 7      | 1          | −1                           | 83                | 35.95             | 84.7                  | 33                |
| 8      | 1          | 0                            | 81.85             | 34.65             | 82                    | 32.5              |
| 9      | 1          | 1                            | 73.55             | 31.4              | 71.8                  | 30.45             |

## 4. Results and Discussion

### 4.1. Sample Characterization

The studied cobalt-rich ferromanganese crusts are dark brown to black in color, with a botryoidal to current-smoothed surface. The botryoids vary in size from millimetric to centimetric, characteristic of hydrogenetic growth, which occurs through slow precipitation from cold seawater. Cross sections of the samples reveal finely laminated growth, forming two to three distinct layers (Figure 3A). Polished thin sections examined under a reflected light microscope show two primary internal structures within the ferromanganese crusts: dendritic to mottled (Figure 3B) and columnar to densely parallel (Figure 3C). The crusts' mineralogy is dominated by poorly crystalline Fe and Mn oxyhydroxides, with Fe-vernadite ( $(\text{Mn}^{4+}, \text{Fe}^{3+}, \text{Ca}, \text{Na})(\text{O}, \text{OH})_2 \cdot n\text{H}_2\text{O}$ ) being the primary mineral, constituting 70–90%

of the composition. Vernadite, a poorly crystalline mineral, is identified primarily by its reflections at 2.45 and 1.72 Å.

Other manganese minerals, present in minor quantities, include birnessite and asbolane, while Fe minerals are represented by the goethite group. Detrital and authigenic minerals are also present, such as quartz, feldspar, and clays, with calcite typically originating from bioclastic accumulation. These minerals form light-colored laminae interspersed with oxyhydroxide minerals.

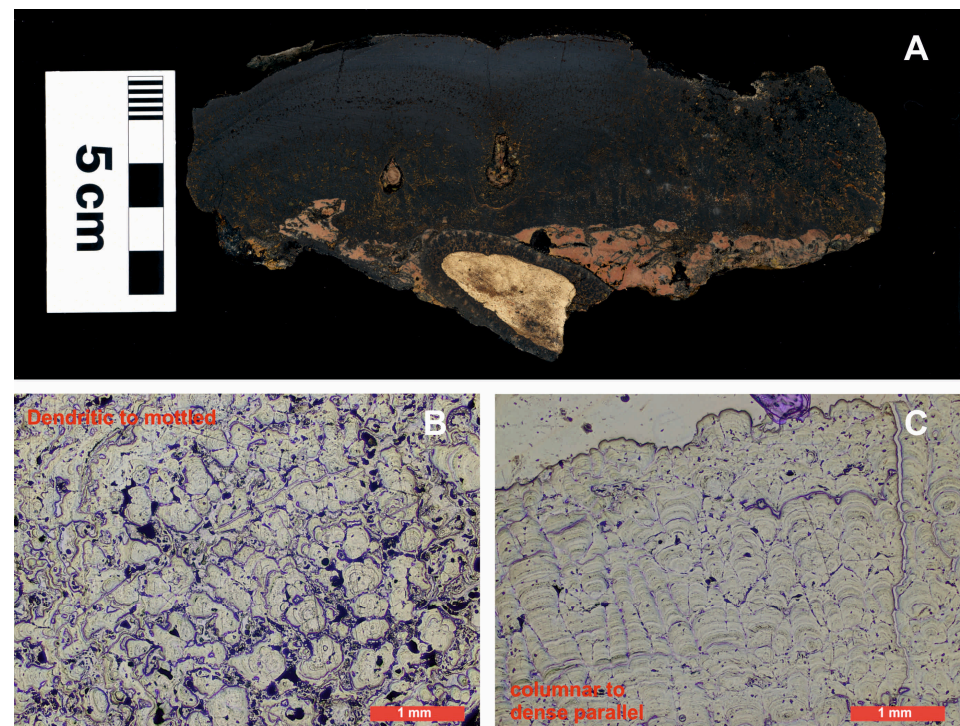


**Figure 3.** (A) Crosscut section of Co-rich ferromanganese crust SUBVENT 1/DA06-4. (B,C) Photomicrographs of characteristic internal textures—dendritic-mottled and columnar-dense parallel, respectively. Canary Islands Seamounts Province.

The geochemistry of the samples studied, Drago 0511/DR04-15 and Subvent 1/DA06-4, aligns with the mineralogical results, showing the highest contents of Fe and Mn (averaging 19.6 wt.% and 19.5 wt.% respectively) among the major elements. The aluminum-silicate elements have a total average of 19 wt.%, with the highest content observed in the deepest sample (SUBVENT 1/DA06-4), which also exhibits a significant input of detrital minerals, as confirmed by the XRD analysis (Table 5). In contrast, the sample DRAGO 0511/DR04-15 shows higher concentrations of CaO and P<sub>2</sub>O<sub>5</sub> (6.05 wt.% and 2.47 wt.% respectively), linked to the presence of phosphates (CFA), also identifiable in the mineralogical analysis.

**Table 5.** Bulk mineralogy of studied samples. 10 Å Mn-oxide represented by todorokite, asbolane, and/or busserite, CFA = carbonate-fluorapatite.

| Sample             | Main Minerals                   | Accessory Minerals                           |
|--------------------|---------------------------------|----------------------------------------------|
| DRAGO 0511/DR04-15 | vernadite, birnessite, goethite | Quartz, calcite, CFA, clay                   |
| SUBVENT 1/DA06-4   | vernadite, birnessite, goethite | 10 Å Mn-oxides, quartz, feldspars, CFA, clay |

Fe-Mn crusts, due to their genetic processes and mineralogy, concentrate high contents of critical and strategic elements. Between them the most enriched are Co, Ni, Cu, V, Mo, and REY, with an average of 3300, 2600, 900, 800, 380, and 2300 µg/g, respectively (See Table 6)

**Table 6.** Bulk chemistry of samples in selected elements for this study.

| Sample             | Fe wt% | Mn wt% | Co µg/g | Ni µg/g | Cu µg/g | REE + Y µg/g |
|--------------------|--------|--------|---------|---------|---------|--------------|
| DRAGO 0511/DR04-15 | 19.9   | 14.5   | 4262    | 2359    | 474     | 2298         |
| SUBVENT 1/DA06-4   | 19.4   | 15.7   | 2424    | 2844    | 1342    | 2323         |
| Mean               | 19.7   | 15.1   | 3343    | 2602    | 908     | 2311         |

#### 4.2. Effect of Variables

Principal components analysis reveals that the factors of time (min) and the ferromanganese crust/Fe(res) ratio have a significant effect, as variations in their levels impact the response differently. This is evident from the main effects plots for Mn and Co extraction shown in Figures 4 and 6, respectively. The main effects analysis indicates that for both samples, S1 and S2, as well as for both Mn and Co extraction, time is directly proportional to mineral extraction, whereas the ferromanganese crust/Fe(res) ratio is inversely proportional to mineral extraction.

Leaching time is directly correlated with an increase in mineral recovery percentage, as the extended duration allows for the complete progression of the chemical and physical reactions that drive mineral dissolution. This phenomenon is primarily attributed to the inherently gradual nature of chemical reactions. Specifically, as the duration increases, the molecules of the leaching agent have more opportunities to interact with the target mineral, thereby improving the extraction efficiency of the desired metal. Several additional factors contribute to this behavior: (i) Reagent diffusion: the leaching agent penetrates the mineral more effectively over time; (ii) Dissolution of less reactive minerals: certain minerals, which require more time for complete dissolution, are progressively broken down; (iii) Dilution of reaction products: prolonged leaching can dilute the concentration of reaction products, such as metal ions in the solution, enabling reactions to continue with greater efficiency; and (iv) Secondary processes: extended leaching times may activate secondary mechanisms, such as the oxidation of accompanying elements or the breakdown of passivating layers, improving mineral exposure to the leaching agent.

In contrast, the recovery rates of Co and Mn decline as the scale-to-iron ratio increases, due to several factors that affect the interaction between the target mineral and the leaching agent. For example: (i) Insufficient reagent concentration: as the quantity of mineral increases without a proportional rise in the leaching agent, the reagent becomes spread too thinly across a larger number of particles, potentially leading to inadequate concentrations for complete metal dissolution; (ii) Reduced mixture uniformity: at higher mineral concentrations, the mixture may become less homogenous, hindering the leaching agent's ability to effectively interact with the mineral particles, thereby reducing process efficiency; and (iii) Solution saturation: a larger quantity of mineral may release more metal ions into the solution, increasing the concentration of dissolved constituents. This can result in solution saturation, impairing the leaching agent's capacity to further dissolve the metal.

Overall, these factors highlight the delicate balance required to optimize leaching conditions for maximum recovery efficiency. Contour graphs (see Figures 5 and 7), on the other hand, show that the maximum Mn extraction is reached at higher time levels and lower to medium levels of ferromanganese crust/Fe(res) ratio (both samples S1 and S2), while the maximum Co extraction is also reached at higher time levels and lower ferromanganese crust/Fe(res) ratio levels (also both samples S1 and S2).

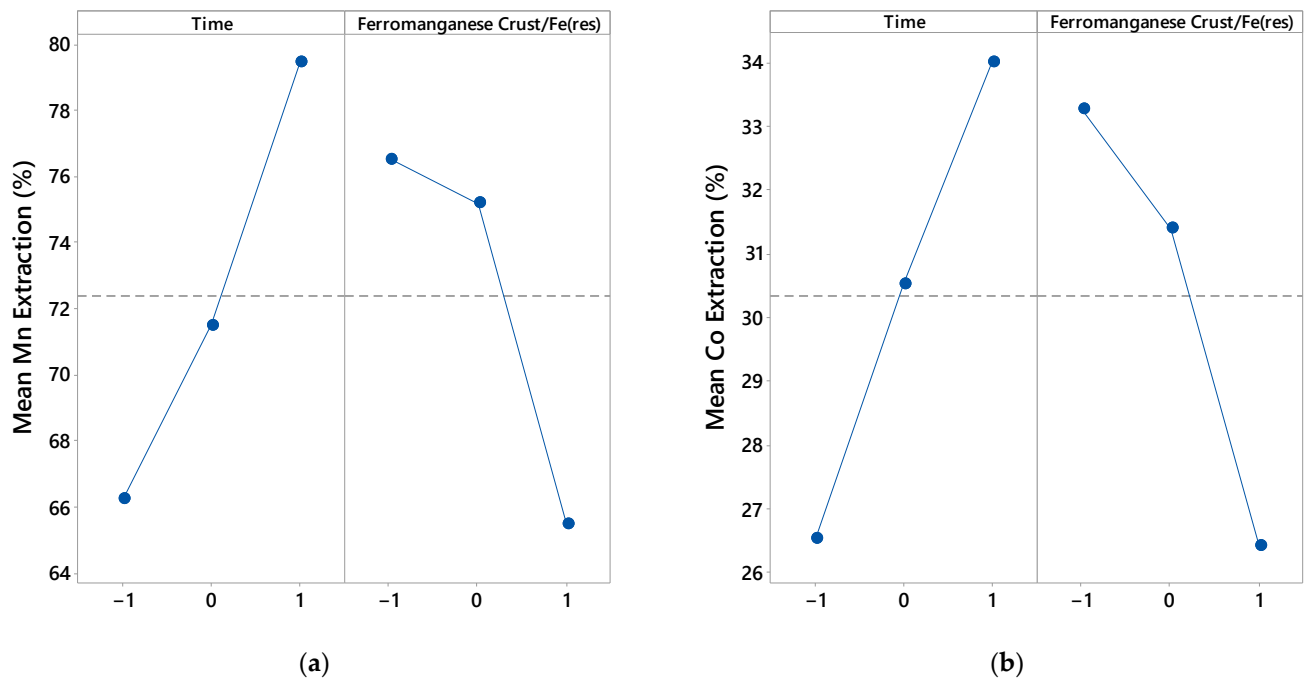


**Figure 4.** Linear main effect plot for Mn (a) and Co (b) extraction (%) [S1].

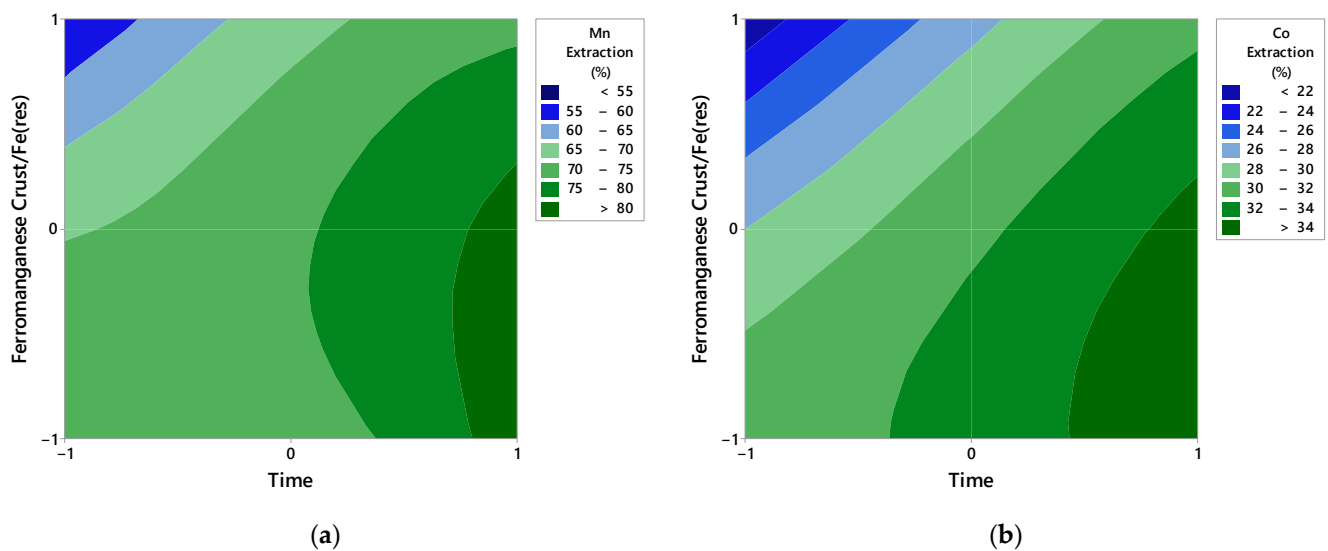


**Figure 5.** Contour plot of Mn (a) and Co (b) Extraction (%) versus ferromanganese crust/Fe(res) and time (min) [S1].

Developing the ANOVA test and the multiple regression adjustment (see Table 7), the Mn and Co extraction for samples S1 and S2 according to the predictive variables of time and ferromanganese crust/Fe(res) ratio is given by Equations (2)–(5), respectively.

It was observed that Mn extraction can be described by multiple linear regression for S1 and quadratic regression for S2, with the interaction factor not contributing significantly to the variability of the model. In contrast, for Co extraction, the quadratic time factor and interaction factor are significant for the S1 model, while only the interaction factor is significant in the S2 model. The ANOVA test indicates that the models adequately represent Mn and Co extraction for the sampled values. Furthermore, the models do not require additional adjustments and are validated by the following goodness-of-fit statistics:

- The  $p$ -values of the models ( $p < 0.05$ ) confirm their statistical significance.

- The  $R^2$  statistic demonstrates that a substantial proportion of the total variability is explained by the models.
- The F-test results (Table 8) show the models' significance, as the F-values from the regressions are significantly greater than the critical F-values for all fitted models.

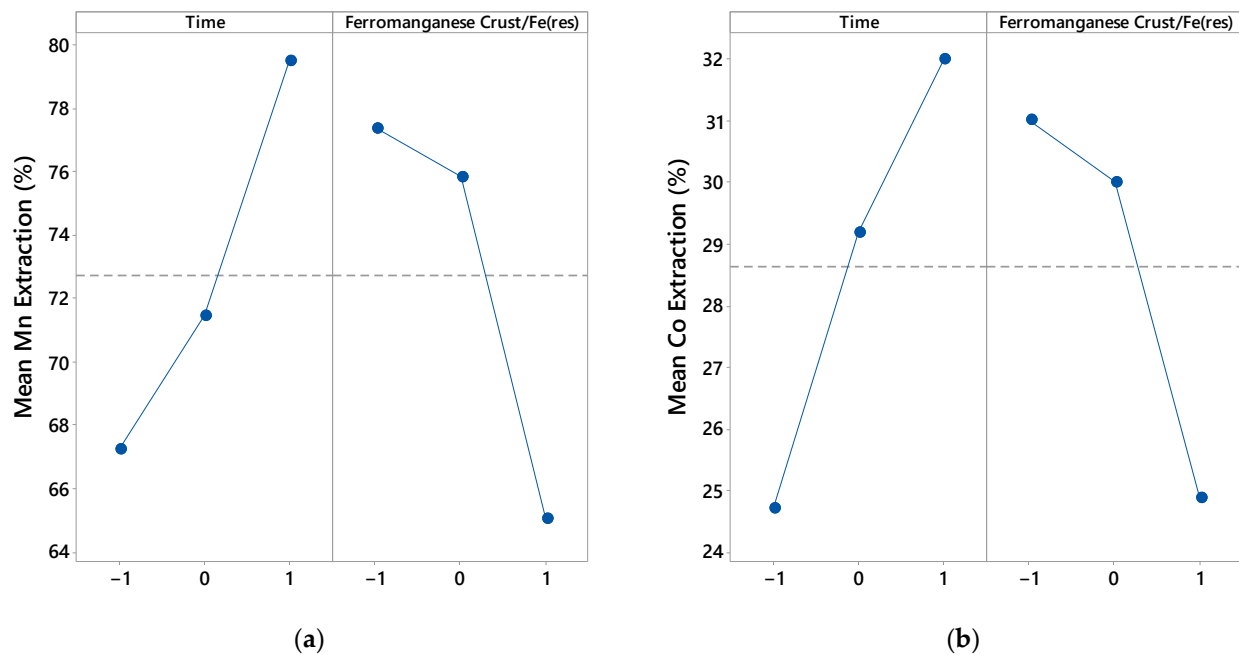


Figure 6. Linear main effect plot for Mn (a) and Co (b) extraction (%) [S2].

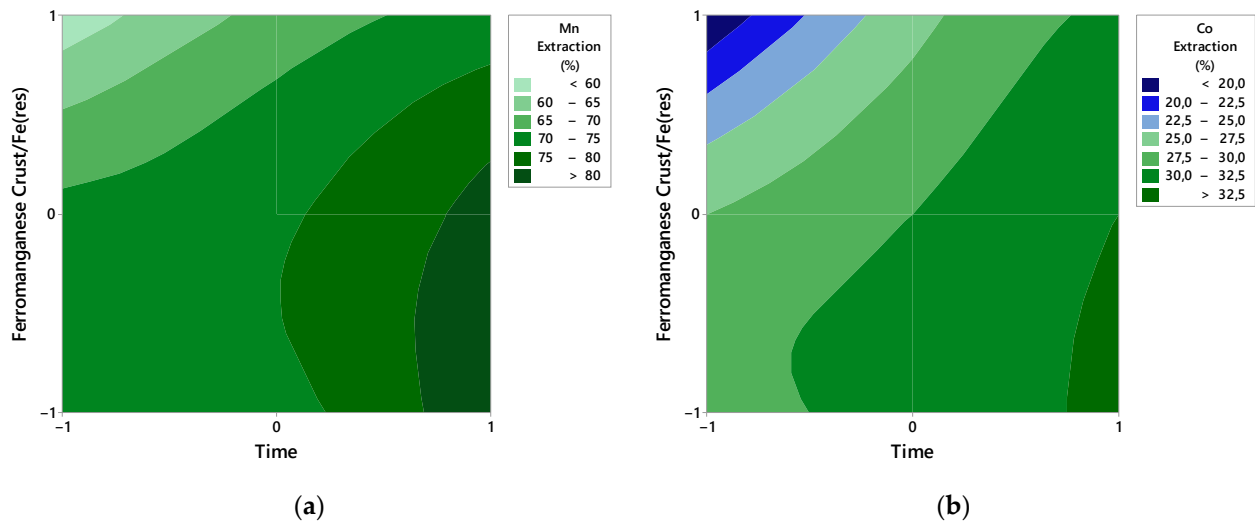


Figure 7. Contour plot of Mn (a) and Co (b) Extraction (%) versus ferromanganese crust/Fe(res) and time (min) [S2].

Table 7. Regression models fitted for Mn and Co extraction (%).

| Sample | Regression Model                                                          | $R^2$ (%) | Equation |
|--------|---------------------------------------------------------------------------|-----------|----------|
| S1     | $Mn\ Ext. (\%) = 72.39 + 6.62x_1 - 5.54x_2$                               | 82.64     | (2)      |
| S1     | $Co\ Ext. (\%) = 31.383 + 3.742x_1 - 3.425x_2 - 1.558x_1^2 + 1.475x_1x_2$ | 98.86     | (3)      |
| S2     | $Mn\ Ext. (\%) = 75.82 + 6.13x_1 - 6.18x_2 - 4.64x_2^2$                   | 92.89     | (4)      |
| S2     | $Co\ Ext. (\%) = 28.622 + 3.642x_1 - 3.067x_2 + 2.212x_1x_2$              | 90.30     | (5)      |

**Table 8.** ANOVA statistics for Mn and Co extraction models for both samples S1 and S2.

| Equation | F-Value | p-Value | S       | Critical F-Value |
|----------|---------|---------|---------|------------------|
| (2)      | 14.28   | 0.005   | 3.95919 | 5.14             |
| (3)      | 87.07   | 0.000   | 0.69439 | 19.24            |
| (4)      | 21.77   | 0.003   | 2.76168 | 5.41             |
| (5)      | 15.52   | 0.006   | 1.82772 | 5.41             |

Additionally, the residual normality test indicates that the residuals are normally distributed. The  $p$ -value of the Kolmogorov-Smirnov (KS) test ( $p > 0.15$ ) exceeds the significance level, and the KS statistics are lower than the critical KS indicator (Table 9). Consequently, the assumption of normality for the regression model residuals cannot be rejected.

**Table 9.** Residuals study for Mn and Co extraction (%).

| Equation | $\mu$    | $\sigma$ | KS    | Critical KS | Normality Test of Residuals<br>(p-Value) |
|----------|----------|----------|-------|-------------|------------------------------------------|
| (2)      | −0.02379 | 1.075    | 0.185 | 0.453       | >0.15                                    |
| (3)      | −0.05316 | 1.098    | 0.143 | 0.453       | >0.15                                    |
| (4)      | 0.02917  | 1.038    | 0.174 | 0.453       | >0.15                                    |
| (5)      | −0.18040 | 1.140    | 0.097 | 0.453       | >0.15                                    |

Gradient analysis of Mn and Co extraction,  $\nabla$ Mn and  $\nabla$ Co extraction ( $x_1$ ,  $x_2$ ) (see Table 10), indicates the increases and decreases in the response variable in function of the predictor variables. The response decreases with respect to the variable  $x_1$  and increases with respect to the variable  $x_2$  for Mn extraction for both samples S1 and S2, for the entire set of sampled variables. However, although the trend is usually maintained for Co extraction, there is an exception in the trend of gradient of  $x_1$  levels for lower levels of  $x_2$  (for sample S1), where the gradient is positive for lower and medium values of time and negative for higher time values.

**Table 10.** Gradient analysis for Mn and Co extraction (%) of Equations (2) to (5).

| Sample S1 | $\nabla$ Mn Extraction (%) [Equation (2)] |             |             |              | $\nabla$ Co Extraction (%) [Equation (3)] |             |             |             |
|-----------|-------------------------------------------|-------------|-------------|--------------|-------------------------------------------|-------------|-------------|-------------|
|           | Levels $x_1 x_2$                          | −1          | 0           | 1            | Levels $x_1 x_2$                          | −1          | 0           | 1           |
|           | −1                                        | (6.6; −5.5) | (6.6; −5.5) | (6.6; −5.5)  | −1                                        | (5.4; −4.9) | (6.9; −4.9) | (8.3; −4.9) |
|           | 0                                         | (6.6; −5.5) | (6.6; −5.5) | (6.6; −5.5)  | 0                                         | (2.3; −3.4) | (3.7; −3.4) | (5.2; −3.4) |
| Sample S2 | 1                                         | (6.6; −5.5) | (6.6; −5.5) | (6.6; −5.5)  | 1                                         | (−0.8; −2)  | (0.6; −2)   | (2.1; −2)   |
|           | $\nabla$ Mn Extraction (%) [Equation (4)] |             |             |              | $\nabla$ Co Extraction (%) [Equation (5)] |             |             |             |
|           | Levels $x_1 x_2$                          | −1          | 0           | 1            | Levels $x_1 x_2$                          | −1          | 0           | 1           |
|           | −1                                        | (6.1; 3.1)  | (6.1; −6.2) | (6.1; −15.5) | −1                                        | (5.9; −5.3) | (3.6; −5.3) | (1.4; −5.3) |
| Sample S2 | 0                                         | (6.1; 3.1)  | (6.1; −6.2) | (6.1; −15.5) | 0                                         | (5.9; −3.1) | (3.6; −3.1) | (1.4; −3.1) |
|           | 1                                         | (6.1; 3.1)  | (6.1; −6.2) | (6.1; −15.5) | 1                                         | (5.9; −0.9) | (3.6; −0.9) | (1.4; −0.9) |

As shown in previous research [10,12], in a leaching process conducted in an acidic medium with the addition of iron as a reducing agent, the potential range for manganese dissolution is 1.4 to 1.2 V, with a pH range of 2 to 8. For Co dissolution, the potential range is 0.8 to 0.25 V, and the pH range is 2 to 4.5. Therefore, the results presented in Figure 8 fall within the appropriate potential and pH ranges to facilitate the regeneration of  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  ions, enabling the simultaneous dissolution of both elements.

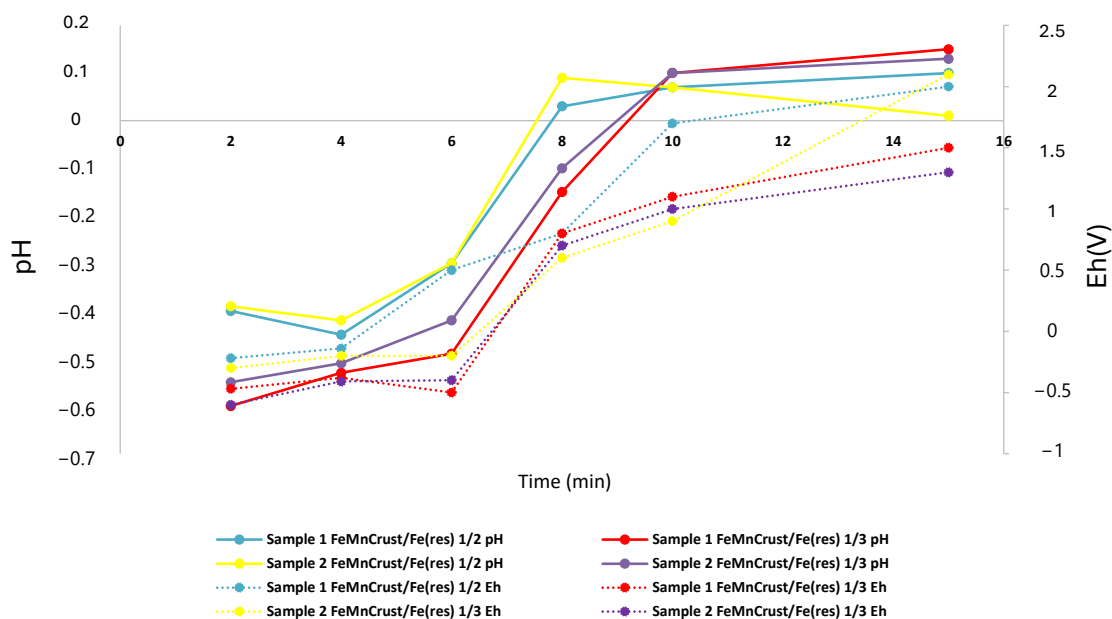


**Figure 8.** Effect of potential and pH on the extraction of Mn and Co from ferromanganese crusts.

#### 4.3. Residue Analysis

Waste from the two samples analyzed does not show the presence of contaminating elements, specifically Fe precipitations. Furthermore, according to the previous study by Pérez et al. [12], the high concentration of ferric and ferrous ions in the system allows it to operate within redox and pH ranges that favor manganese dissolution, preventing its precipitation.

##### 4.3.1. DRAGO 0511/DR04-15

Figure 9 shows a micrograph obtained via SEM-EDS, used to identify elemental associations. The image reveals particles with Fe/S/O and Si/S/O associations, as well as impurities with Fe/O, Al/Si/O, and Mg/Si/O associations. The Si/S/O particles range in size from 29.0  $\mu\text{m}$  to 48.8  $\mu\text{m}$  in length, while the Fe/S/O particles range from 7.6  $\mu\text{m}$  to 30.1  $\mu\text{m}$  in length.

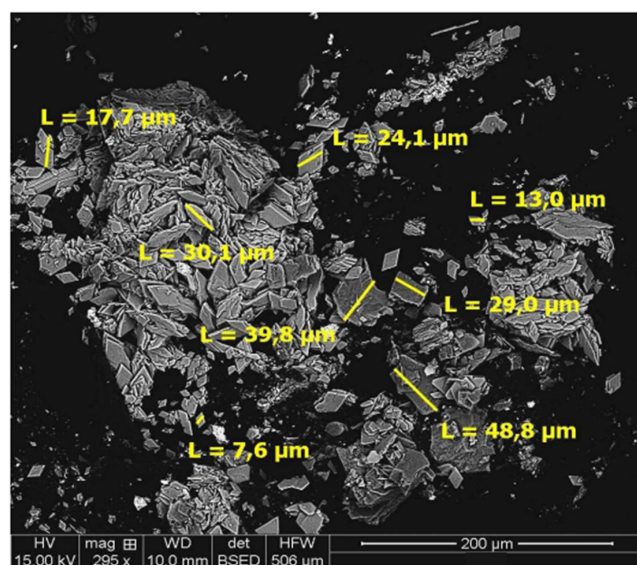


**Figure 9.** Scanning electron microscopy (SEM-EDS) micrograph of residue of Drago 0511/DR04-15. Magnification 295 $\times$ .

Figure 10 depicts particles with Fe/S/O associations (orange in (1), green in (2), and gray in (3)) and Si/S/O associations (purple in (1), blue in (2), and pink in (3)). Additionally, impurities with Fe/O associations are shown (lemon green in (1) and (2), and light gray in (3)), as well as Al/Si/O associations (dark green in (1) and uncolored in (2) and (3)) and Mg/Si/O associations (pink in (2), and uncolored in (1) and (3)). The analysis confirms the absence of contaminating elements and demonstrates that no cobalt or manganese compound precipitation occurred (see Figure 11).

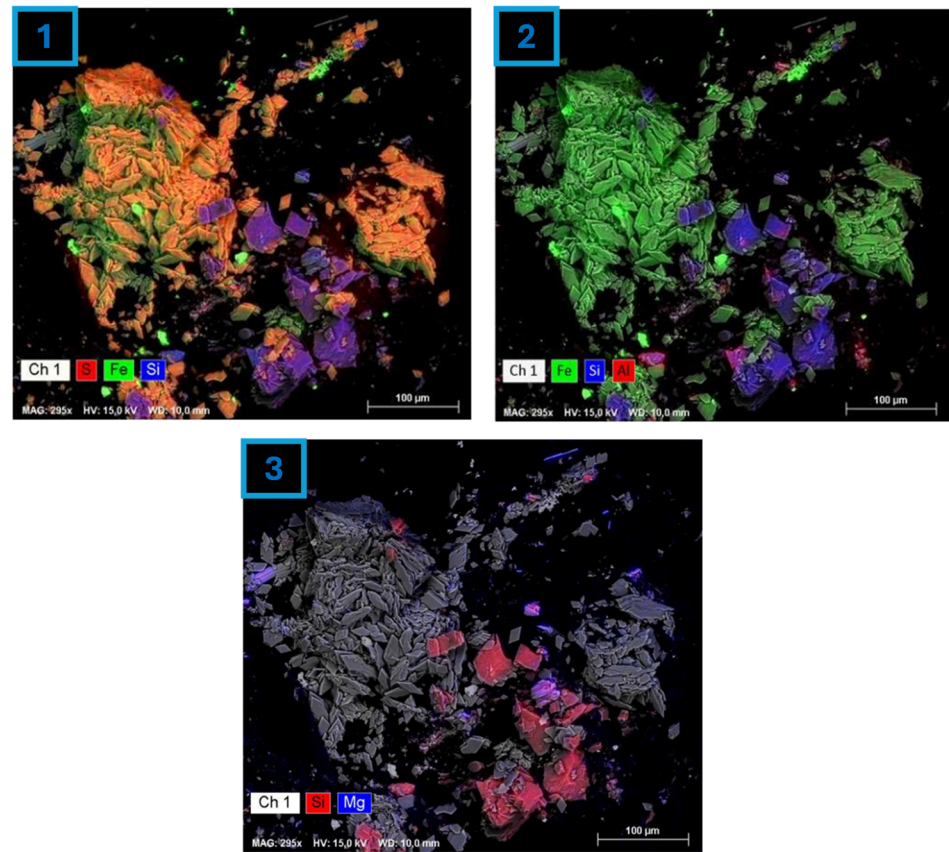
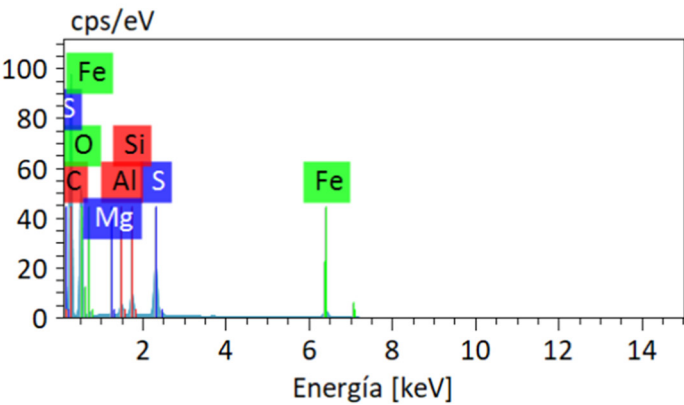


**Figure 10.** SEM micrograph with EDS analysis (color change) of residue Drago 0511/DR04 15. Magnification 295× (100 µm).



| Map     |          |                |                          |
|---------|----------|----------------|--------------------------|
| Element | Mass (%) | Mass Norm. (%) | Abs. Error (%) (1 sigma) |
| O       | 32,82    | 61,98          | 3,43                     |
| S       | 7,86     | 14,85          | 0,3                      |
| Fe      | 7,84     | 14,81          | 0,26                     |
| Si      | 2,79     | 5,27           | 0,14                     |
| Al      | 1,4      | 2,63           | 0,09                     |
| Mg      | 0,25     | 0,46           | 0,04                     |
|         | 52,96    | 100            |                          |

**Figure 11.** Scanning electron microscopy elemental analysis for sample DRAGO 0511/DR04-15 (SEM-EDS).

#### 4.3.2. SUBVENT 1/DA06-4

The micrograph in Figure 12 (obtained via SEM-EDS) displays particles with Fe/S/O and Si/S/O associations, where the Si/S/O particles range in size from 47.1 to 215.9  $\mu\text{m}$  in length. Additionally, the presence of Fe impurities is observed.

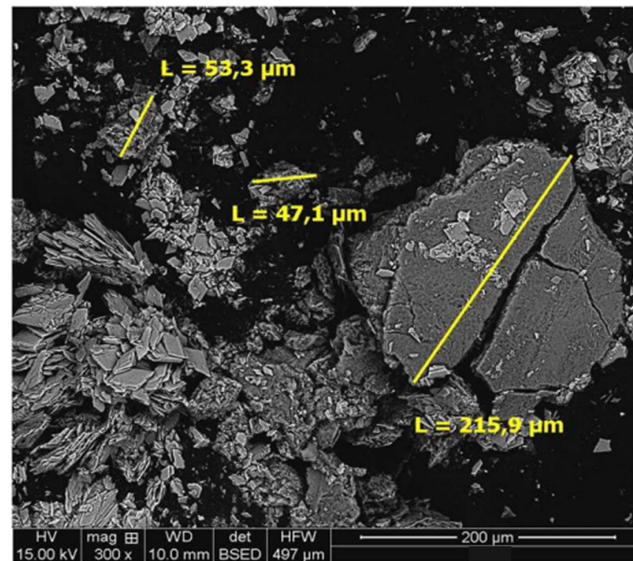


**Figure 12.** Scanning electron microscopy (SEM-EDS) micrograph of residue of Subvent 1/DA064. Magnification 300 $\times$ .

Figure 13 illustrates particles with Si/S/O associations (red in (1), purple in (2) and (3)) and Fe/S/O associations (pink in (1), red in (2), and orange in (3)). Additionally, Fe impurities are identified (blue in (1) and uncolored in (2) and (3)). Similar to Sample 1, this sample shows no evidence of contaminating element formation (see Figure 14).

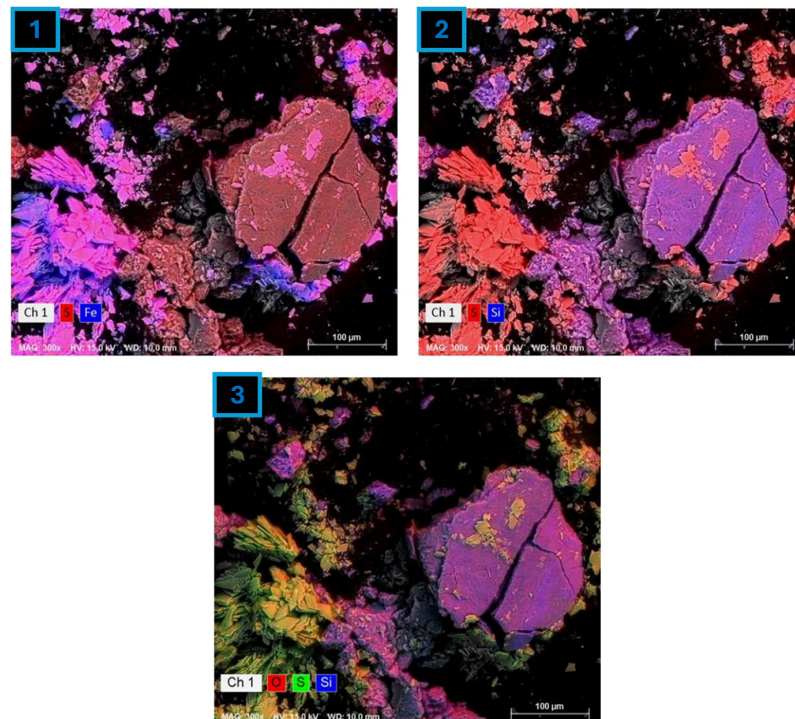


**Figure 13.** SEM micrograph with EDS analysis (color change) of residue Subvent 1/DA064. Magnification 300 $\times$  (100  $\mu\text{m}$ ).

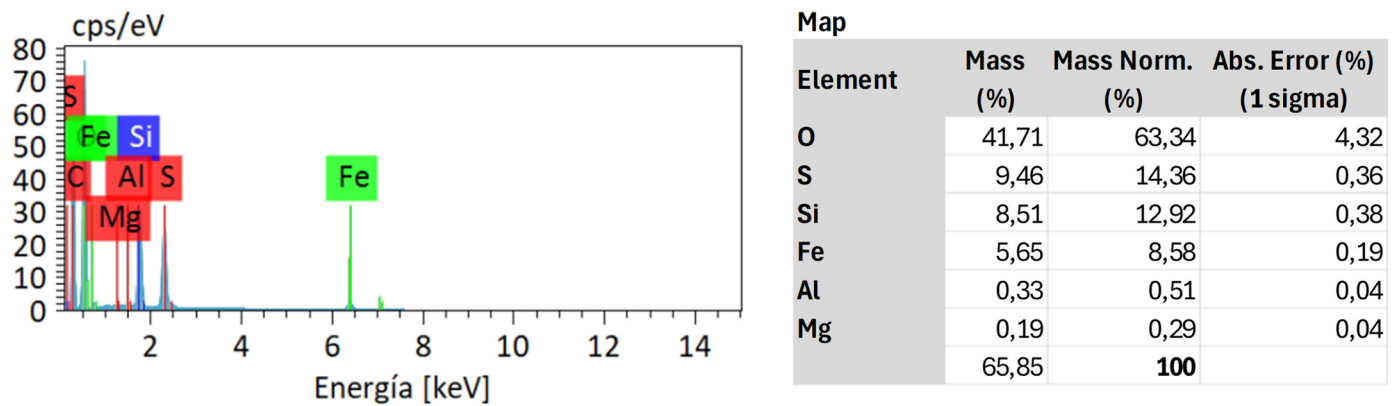


**Figure 14.** Scanning electron microscopy elemental analysis for sample Subvent 1/DA06-4 (SEM-EDS).

## 5. Conclusions

This study presents results obtained through statistical models to investigate Mn and Co extraction in an acid medium at a room temperature of 25 °C. The effects of time and the ferromanganese crust/Fe(res) ratio were studied as predictive variables. The key findings are as follows:

- Mn and Co extraction can be effectively modeled using multiple regression techniques, with strong goodness-of-fit indicators.
- Optimal Mn and Co extraction is achieved at longer durations (30 min) and lower ferromanganese crust/Fe(res) ratios (1/3) for both samples, S1 and S2.
- Gradient analysis shows that Mn and Co extraction for both samples is directly proportional to time and inversely proportional to the ferromanganese crust/Fe(res) ratio in most cases, except for Co extraction at higher time levels and lower ferromanganese crust/Fe(res) ratios.
- No precipitation of Co or Mn species was observed in the studied residues.

While RSM and DOE offer substantial advantages in modeling leaching processes, alternative approaches such as Bayesian statistics and genetic programming could provide valuable additional insights and suggest interesting avenues for future research. Bayesian models, for instance, incorporate probabilistic elements to predict leaching outcomes based on prior and posterior knowledge, offering a novel perspective on process optimization [45]. Similarly, genetic programming can be utilized to develop predictive models for leaching processes, serving as a robust tool for understanding the relationships between process parameters and leaching efficiency [53]. These alternative methodologies could complement RSM and DOE, enabling a more comprehensive understanding of leaching processes.

**Author Contributions:** Writing—original draft and investigation K.P.; Writing—original draft and conceptualization N.T.; formal analysis and methodology, M.M., I.C. and M.S.; writing—review and editing and investigation, I.S. and F.M.G.M.; conceptualization, resources and funding acquisition, F.J.G. and E.M.; formal analysis and supervision, J.C.; investigation; supervision and project administration, P.C.H. All authors have read and agreed to the published version of the manuscript.

**Funding:** This study was funded by the ATLANTIS project (PID2021-124553OB-I00) of the Spanish State Investigation Agency (AEI), European contract EMODnet-Geology (EASME/EMFF/2016/1.31.2-Lot 1/SI2.750862), and the Horizon Europe projects GSEU (HORIZON-CL5-2021-D3-02-14, Project 101075609).

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** The original contributions presented in this study are included in the article. Further inquiries can be directed to the corresponding authors.

**Acknowledgments:** Kevin Perez acknowledges the infrastructure and support of the PhD Program in Mineral Processes Engineering of the Universidad de Antofagasta. The authors are grateful for the support of ANID-Chile through the research projects FONDECYT Iniciación 11230550 and ANID/FONDAP 1522A0006 Solar Energy Research Center SERC-Chile.

**Conflicts of Interest:** The authors declare no conflicts of interest.

## References

1. Toro Villarroel, N.R.; Torres Alborno, D.A. *La Fuerza del Litio*; Universidad Arturo Prat: Iquique, Chile, 2023; ISBN 9789564164717.
2. Koschinsky, A.; Heinrich, L.; Boehnke, K.; Cohrs, J.C.; Markus, T.; Shani, M.; Singh, P.; Smith Stegen, K.; Werner, W. Deep-Sea Mining: Interdisciplinary Research on Potential Environmental, Legal, Economic, and Societal Implications. *Integr. Environ. Assess. Manag.* **2018**, *14*, 672–691. [\[CrossRef\]](#)
3. Mohammadi, A.; Fazeli, A. Future Market and Challenges of Lithium/Sulfur Batteries. In *Nanostructured Materials for Lithium/Sulfur Batteries*; Springer International Publishing: Cham, Switzerland, 2024; pp. 697–721.
4. Olivetti, E.A.; Ceder, G.; Gaustad, G.G.; Fu, X. Lithium-Ion Battery Supply Chain Considerations: Analysis of Potential Bottlenecks in Critical Metals. *Joule* **2017**, *1*, 229–243. [\[CrossRef\]](#)
5. Naseri, T.; Pourhossein, F.; Mousavi, S.M.; Kaksonen, A.H.; Kuchta, K. Manganese Bioleaching: An Emerging Approach for Manganese Recovery from Spent Batteries. *Rev. Environ. Sci. Biotechnol.* **2022**, *21*, 447–468. [\[CrossRef\]](#)
6. Habib, K.; Hansdóttir, S.T.; Habib, H. Critical Metals for Electromobility: Global Demand Scenarios for Passenger Vehicles, 2015–2050. *Resour. Conserv. Recycl.* **2020**, *154*, 104603. [\[CrossRef\]](#)
7. Toro, N.; Gálvez, E.; Saldaña, M.; Jeldres, R.I. Submarine Mineral Resources: A Potential Solution to Political Conflicts and Global Warming. *Min. Eng.* **2022**, *179*, 107441. [\[CrossRef\]](#)
8. Gulley, A.L. The Development of China's Monopoly over Cobalt Battery Materials. *Miner. Econ.* **2024**, *37*, 619–631. [\[CrossRef\]](#)
9. Müller, D.; Groves, D.I.; Santosh, M.; Yang, C.-X. Critical Metals: Their Applications with Emphasis on the Clean Energy Transition. *Geosyst. Geoenviron.* **2024**, *4*, 100310. [\[CrossRef\]](#)
10. Pérez, K.; Toro, N.; Robles, P.; Gallegos, S.; Gálvez, E.; González, F.J.; Marino, E.; Hernández, P.C. Cobalt and Manganese Extraction from Ocean Nodules by Co-Processing with Steel Metallurgical Slag. *Metals* **2023**, *13*, 1079. [\[CrossRef\]](#)
11. Torres, D.; Pérez, K.; Galleguillos Madrid, F.M.; Leiva, W.H.; Gálvez, E.; Salinas-Rodríguez, E.; Gallegos, S.; Jamett, I.; Castillo, J.; Saldana, M.; et al. Salar de Atacama Lithium and Potassium Productive Process. *Metals* **2024**, *14*, 1095. [\[CrossRef\]](#)
12. Pérez, K.; Toro, N.; Robles, P.; Galleguillos Madrid, F.M.; Gálvez, E.; González, F.J.; Marino, E.; Castillo, J.; Jamett, I.; Hernández, P.C. Extraction of Cobalt and Manganese from Ferromanganese Crusts Using Industrial Metal Waste through Leaching. *Metals* **2024**, *14*, 1044. [\[CrossRef\]](#)
13. Hein, J.R.; Mizell, K.; Koschinsky, A.; Conrad, T.A. Deep-Ocean Mineral Deposits as a Source of Critical Metals for High- and Green-Technology Applications: Comparison with Land-Based Resources. *Ore Geol. Rev.* **2013**, *51*, 1–14. [\[CrossRef\]](#)
14. Halbach, P.; Marchig, V.; Scherhag, C. Regional Variations in Mn, Ni, Cu, and Co of Ferromanganese Nodules from a Basin in the Southeast Pacific. *Mar. Geol.* **1980**, *38*, M1–M9. [\[CrossRef\]](#)
15. Lusty, P.A.J.; Hein, J.R.; Josso, P. Formation and Occurrence of Ferromanganese Crusts: Earth's Storehouse for Critical Metals. *Elements* **2018**, *14*, 313–318. [\[CrossRef\]](#)
16. Mohwinkel, D.; Kleint, C.; Koschinsky, A. Phase Associations and Potential Selective Extraction Methods for Selected High-Tech Metals from Ferromanganese Nodules and Crusts with Siderophores. *Appl. Geochem.* **2014**, *43*, 13–21. [\[CrossRef\]](#)
17. Konstantinova, N.; Son, V.T.; Thang, L.A.; Trung, T.T.; Giang, V.T.; Dung, N.T.T.; Vanshtein, B.; Cherkashov, G. Ferromanganese Crusts of the Vietnam Margin, Central South China Sea: Composition and Genesis. *Mar. Geol.* **2022**, *453*, 106911. [\[CrossRef\]](#)
18. Mwanat, M.H.M.; Kasongo, K.B. Cobalt Dissolution from Concentrate in Sulfuric Acid—Ferrous Sulfate System: Process Parameters Optimization by Response Surface Methodology (RSM). *J. Sustain. Metall.* **2021**, *7*, 1838–1851. [\[CrossRef\]](#)
19. Muthalib, N.; Abdullah, N.; Ismail, S. Reductive leaching of low grade manganese ore (lgmo) using glucose in sulphuric acid: Optimization condition using response surface methodology. *ASEAN Eng. J.* **2018**, *8*, 64–73. [\[CrossRef\]](#)
20. Mbuya, B.; Mulaba-Bafubandi, A.F. Predicting Optimized Dissolution of Selected African Copperbelt Copper-Cobalt-Bearing Ores by Means of Neural Network Prediction and Response Surface Methodology Modeling. *Process Integr. Optim. Sustain.* **2023**, *7*, 583–597. [\[CrossRef\]](#)
21. Mathaba, M.; Banza, J.C. Application of Machine Learning Approach (Artificial Neural Network) and Shrinking Core Model in Cobalt (II) and Copper (II) Leaching Process. *J. Environ. Sci. Health Part A* **2024**, *59*, 25–32. [\[CrossRef\]](#)
22. Yu, B.; Zhan, D.; Liu, J.; Wang, H.; Yang, S.; Hu, X. Response Surface Method Optimization to Improve Copper Extraction from Refractory Copper Oxide Ore. *Min. Met. Explor.* **2022**, *39*, 2221–2228. [\[CrossRef\]](#)

23. Salehi, S.; Noaparast, M.; Shafaei, S.Z. Response Surface Methodology (RSM) for Optimization of Chalcopyrite Concentrate Leaching with Silver-Coated Pyrite. *Physicochem. Probl. Miner. Process.* **2016**, *52*, 1023–1035. [\[CrossRef\]](#)
24. Ayodele, T.J.; Daniyan, A.A.; Adeleke, A.A.; Ola-Omole, O.O. Optimization of Leaching Parameters for the Extraction of Copper from Hematite-Dominated Copper Ore Using Response Surface Methodology (RSM). *Niger. J. Technol.* **2023**, *42*, 353–363. [\[CrossRef\]](#)
25. Asl, M.D.; Salahshoori, I.; Seyfaee, A.; Hatami, A.; Golbarari, A.A. Experimental Results and Optimization via the Design of Experiment (DOE) of the Copper Ion Recovery from Aqueous Solutions Using Emulsion Liquid Membrane (ELM) Method. *Desalination Water Treat.* **2020**, *204*, 238–256. [\[CrossRef\]](#)
26. Rajendran, S.; Vakamalla, T.R.; Mangadoddy, N. Numerical Methods in Mineral Processing: An Overview. *Miner. Process. Benef. Oper. Process Optim. Through Model.* **2023**, 251–285. [\[CrossRef\]](#)
27. Cisternas, L.A.; Lucay, F.A.; Botero, Y.L. Trends in Modeling, Design, and Optimization of Multiphase Systems in Minerals Processing. *Minerals* **2019**, *10*, 22. [\[CrossRef\]](#)
28. Castillo-Villagra, R.; Icarte, G.; Thoben, K.D. Modelling the Make Process of the Mineral Supply Chain Upstream Segment. *Resources* **2023**, *12*, 132. [\[CrossRef\]](#)
29. Noome, Z.M.; le Roux, J.D.; Padhi, R. Optimal Control of Mineral Processing Plants Using Constrained Model Predictive Static Programming. *J. Process Control* **2023**, *129*, 103067. [\[CrossRef\]](#)
30. Bourgeois, F.; Julcour-Lebigue, C.; Cassayre, L.; Bailly, F.; Cyr, M.; Touzé, S. Guiding Mineralization Process Development with Geochemical Modelling. In Proceedings of the GHGT 2018—14th International Conference on Greenhouse Gas Control Technologies, Melbourne, Australia, 21–26 October 2018. [\[CrossRef\]](#)
31. Yakovlev, B.V.; Nikiforova, L.V. Mathematical Modeling of a Particle Motion in Mineral Processing Devices. *AIP Conf. Proc.* **2021**, *2328*, 030004. [\[CrossRef\]](#)
32. Parian, M.; Lamberg, P.; Rosenkranz, J. Process Simulations in Mineralogy-Based Geometallurgy of Iron Ores. *Miner. Process. Extr. Metall. Trans. Inst. Min. Metall.* **2021**, *130*, 25–30. [\[CrossRef\]](#)
33. Straka, M.; Saderova, J.; Bindzar, P. Simulation and Modelling of Transport Processes for the Needs of Mineral Resources Delivery Support. In Proceedings of the 4th EAI International Conference on Management of Manufacturing Systems, Krynica-Zdrój, Poland, 8–10 October 2019; EAI/Springer Innovations in Communication and Computing; Springer International Publishing: Cham, Switzerland, 2020; pp. 93–101. [\[CrossRef\]](#)
34. Zuo, Y.; Zhang, W.; Che, J.; Feng, S.; Chen, Y.; Wang, C. Efficient Extraction of Cobalt and Copper: Leveraging Redox Chemistry in Oxide and Sulfide Copper-Cobalt Ores. *Sep. Purif. Technol.* **2025**, *354*, 128671. [\[CrossRef\]](#)
35. Ju, J.; Feng, Y.; Li, H.; Ma, R.; Li, Y.; Zhao, H.; Wang, H.; Jiang, S. An Innovative Method for the Efficient and Selective Extraction of Co, Ni, Cu, and Mn from Oceanic Cobalt-Rich Crusts by Ammonium Sulfate Roasting: Behavior, Roasting Kinetics and Mechanism. *Min. Eng.* **2024**, *207*, 108543. [\[CrossRef\]](#)
36. Zhang, M.; Zhu, G.; Zhao, Y.; Feng, X. A Study of Recovery of Copper and Cobalt from Copper–Cobalt Oxide Ores by Ammonium Salt Roasting. *Hydrometallurgy* **2012**, *129–130*, 140–144. [\[CrossRef\]](#)
37. Yu, D.; Zhang, C.; Guo, X.; Tian, Q.; Cui, F.; Gan, X. Method for Extracting and Treating Copper-Cobalt Alloy by Utilizing Metal Melt. Chinese Patent No. CN111172399A, 19 May 2020.
38. da Silveira Leite, D.; Carvalho, P.L.G.; de Lemos, L.R.; Mageste, A.B.; Rodrigues, G.D. Hydrometallurgical Separation of Copper and Cobalt from Lithium-Ion Batteries Using Aqueous Two-Phase Systems. *Hydrometallurgy* **2017**, *169*, 245–252. [\[CrossRef\]](#)
39. Xu, K.; Deng, Q.; Su, T.; Tan, T.; Wang, C.; Chen, L. The Extracting Method of Tough Cathode is Extracted in a Kind of Cobalt Concentrate. Chinese Patent No. CN110318072A, 11 October 2019.
40. Yang, J.; Xu, W.; Zhang, S.; Chen, J.; Sun, H. Production Method for Extracting Cobalt from Copper Extraction Tail Liquid. Chinese Patent No. CN111286607A, 16 June 2020.
41. Bampole, D.L.; Mulamba, E.L. Mathematical Modeling for Enhancement Heap Leaching of D.M.S Tailings for the Recovering Copper and Cobalt: Using Taguchi Method and Analysis Variance. *IOSR J. Appl. Chem.* **2017**, *10*, 50–57. [\[CrossRef\]](#)
42. Xiao, B.Q.; Jiang, F.; Peng, J.H.; Ju, S.H.; Zhang, L.H.; Yin, S.H.; Zhang, L.B.; Xu, L.; Tian, S.H. Optimization Study of Operation Parameters for Extracting Cu<sup>2+</sup> from Sulfuric Solution Containing Co<sup>2+</sup> with LIX984N in a Laminar Microchip. *Arab. J. Sci. Eng.* **2018**, *43*, 2145–2153. [\[CrossRef\]](#)
43. Sobhi Amjad, R.; Asadollahzadeh, M.; Torkaman, R.; Torab-Mostaedi, M. Optimizing the Extraction of Cobalt Ions under Response Surface Methodology and without Organic Solutions. *Can. J. Chem. Eng.* **2023**, *101*, 3532–3540. [\[CrossRef\]](#)
44. Movahhedi, H.; Mohammad Beygian, A.; Keshavarz Alamdari, E.; Moradkhani, D. Developing of a Counter-Current Copper Leaching Process Using Response Surface Methodology. *Miner. Process. Extr. Metall. Rev.* **2024**, *45*, 1–11. [\[CrossRef\]](#)
45. Mbuya, B.; Meta-Mvita, J.; Mulaba-Bafubandi, A.F. Bayesian Statistics Study of a Sustainable Dissolution of Cobalt-Bearing Minerals from Cu-Co Ores. *Can. J. Chem. Eng.* **2023**, *101*, 5832–5843. [\[CrossRef\]](#)
46. Lasheen, T.; Elenein, S.A.A.; Saleh, W.A.; Orabi, A.H.; Ismaiel, D.A. Reductive Leaching Kinetics of Low Grade Manganese Deposits in H<sub>2</sub>SO<sub>4</sub> Solution Using Malonic Acid as Reducing Agent. *Int. J. Sci. Basic Appl. Res. (IJSBAR)* **2014**, *15*, 151–163.

47. van den Bogaard, P. The Origin of the Canary Island Seamount Province—New Ages of Old Seamounts. *Sci. Rep.* **2013**, *3*, 2107. [\[CrossRef\]](#)
48. Somoza, L. *Presentación Parcial de Datos e Información Sobre los Límites de la Plataforma Continental de España al Oeste de las Islas Canarias, Conforme a la Parte vi y El Anexo Ii de la Convención de las Naciones Unidas Sobre el Derecho del Mar*; Instituto Geológico y Minero de España: Madrid, Spain, 2014.
49. Montgomery, D.C. *Design and Analysis of Experiments*, 8th ed.; John Wiley & Sons: New York, NY, USA, 2012; ISBN 978-1-118-14692-7.
50. Ghosh, M.K.; Barik, S.P.; Anand, S. Sulphuric Acid Leaching Of Polymetallic Nodules Using Paper As A Reductant. *Trans. Indian. Inst. Met.* **2008**, *61*, 477–481. [\[CrossRef\]](#)
51. Mitić, M.; Tošić, S.; Pavlović, A.; Mašković, P.; Kostić, D.; Mitić, J.; Stevanović, V. Optimization of the Extraction Process of Minerals from *Salvia officinalis* L. Using Factorial Design Methodology. *Microchem. J.* **2019**, *145*, 1224–1230. [\[CrossRef\]](#)
52. Mathews, P.G. *Design of Experiments with MINITAB*; Tony, W.A., Ed.; ASQ Quality Press: Milwaukee, MI, USA, 2005; ISBN 0873896378.
53. Ebrahimzade, H.; Khayati, G.R.; Schaffie, M. A Novel Predictive Model for Estimation of Cobalt Leaching from Waste Li-Ion Batteries: Application of Genetic Programming for Design. *J. Environ. Chem. Eng.* **2018**, *6*, 3999–4007. [\[CrossRef\]](#)

**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.