

Review

# Manganese Nodules in Chile, an Alternative for the Production of Co and Mn in the Future—A Review

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**Abstract:** Given the active growth of emerging technology industries, it has become essential to have large quantities of critical metals to meet the current demand. In the Chilean mining industry, there is a depletion of high-grade mineral ores, and there is hence a need to increase production levels in the copper industry and diversify its market by extracting other elements. One of the strategies is to foster the production of lithium batteries, but the manufacture requires reserves of cobalt (Co) and manganese (Mn). Currently, Co reserves are not being exploited in Chile, and Mn production is almost negligible. This is due to the apparent shortage of high-grade ores on the land surface of the country. Given this scenario, the seabed manganese nodules are presented as a good alternative due to their high average grades of Co and Mn, which in turn would allow the growth of strategic value-added industries including lithium battery production. Chile's current environmental regulations prevent the exploitation of marine resources. However, given technological advances worldwide, both in collection mechanisms and extractive processes, in addition to the needs generated from the future strategic plans, leads us to think about a project to exploit manganese nodules locally.

**Keywords:** manganese nodules; cobalt; manganese; Chilean marine deposits

## 1. Introduction

Critical metals are those that have high supply risk and whose shortfall can have a major economic impact [1]. These metals are essential for the fabrication of high technology, including computer chips, electric vehicles, wind turbines, cellular phones, etc. [2]. There is a constant increase in worldwide consumption, which implies a growth of the various element extractive industries. This generates a depletion of high-grade minerals in the Earth's crust, including gold, cobalt and copper ores, among others [3]. For example, in Chile in 1942, Co grades between 4% and 5% were commonly reported, whereas in 1968, average Co grades were typically 1% or lower. Currently, the grades reach as high as 1.6% in certain parts of the country [4]. Countries where a large part of the income depends on the export of raw materials, such as Chile, where mining contributes an average of 10% of the gross

domestic product [5], are in need of generating alternatives to adapt to this new scenario. Four main strategic points are raised [6]:

- Increased production costs;
- Drive toward increasing production levels to compensate for the drop in grades;
- Diversifying the extraction in consideration of other elements and obtaining byproducts from the main element to be exploited (an example is the enormous growth of the molybdenum industry, which is obtained as a by-product from copper flotation processes);
- Changing the costs of essential resources, such as water and electricity.

Considering the risks of climate change, it is essential to have sufficient quantities of critical metals in order to satisfy current demand levels to assure the fabrication of environmentally friendly technologies [7]. A good example of this is the progressive increase in the purchase of electric vehicles (between the years 2015 and 2018, there was a 400% increase in the purchase of electric cars) [8]. This, in turn, has generated a massive increase in lithium-nickel, lithium-cobalt, and lithium-cobalt-manganese [9] battery technologies, an aspect that opens a window of real opportunity for a diversification of Chilean mining production. In a mineral resources perspective, Chile, has enormous lithium resources, being the second largest producer of this commodity in the world (Chile produced 19,000 tons of lithium in 2019) [10], in addition to its copper reserves. It may therefore be advantageous to extend the high lithium production in Chile into value-added products, including lithium ion batteries. However, this possible future strategy at the national level is hindered by the absence of cobalt and manganese production.

For these aforementioned problems, innovative alternatives emerge that allow the growth of the mining industry to be maintained, and also satisfy the current demand for metals in the world. Deep-sea mining appears as a promising alternative, for the shortage of high-grade elements on the Earth's surface, and the shortage of critical elements [2]. Within these marine resources, there are three main types of deposits—manganese nodules, ferromanganese crusts, and seafloor massive sulphides [11]. As described below, the nodules are typically palm-sized (between 1 cm and 12 cm) with spheroidal or ellipsoidal shapes that are sporadically concentrated over large regions; in contrast, the crusts are porous growths that overly hard-rock seamounts, and the massive sulphide deposits are geologically comparable to the largescale massive sulphides that have long been exploited through terrestrial mining. Chilean marine resources are relatively abundant in manganese nodules [12].

Manganese nodules are a promising alternative source for the extraction of Mn and Co, which could provide the necessary raw materials to boost a lithium battery manufacturing industry in Chile and promote the creation of value-added products.

This manuscript describes the most relevant general aspects of manganese nodules, such as their formation and growth, distribution in the world, mineralogical composition, and collection methods, focusing on the richness of the seabed in Chile, highlighting the importance that manganese nodules may have due to the scarcity of exploitation of Mn and Co resources in the country, and their strategic importance for the future of its industry. Finally, the different mechanisms of extraction of Mn and Co from manganese nodules are detailed.

## 2. Manganese Nodules

Manganese nodules, also called polymetallic nodules, were first discovered during the Challenger expedition between the years 1872–1876 [6]. These mineral resources are rocky concretions with a spherical shape and a brownish black color; they consist of concentric layers of Fe and Mn hydroxides, with sizes ranging between 1 cm and 12 cm [13] (see Figure 1). These form groups of metallic oxide concretions dispersed in the sedimentary zone of the seabed of the Pacific, Atlantic, and Indian Oceans, at depths of 4500 m, reaching reserves of 1–3 trillion tons [14]. These may have economic potential due to the high concentrations of Mn, Co, Ni, Te, Ti, Pt, and rare earth elements (REE) [15,16].

Therefore, the future extraction of critical elements from manganese nodules may be essential for the rapid growth of the technology industry [17].



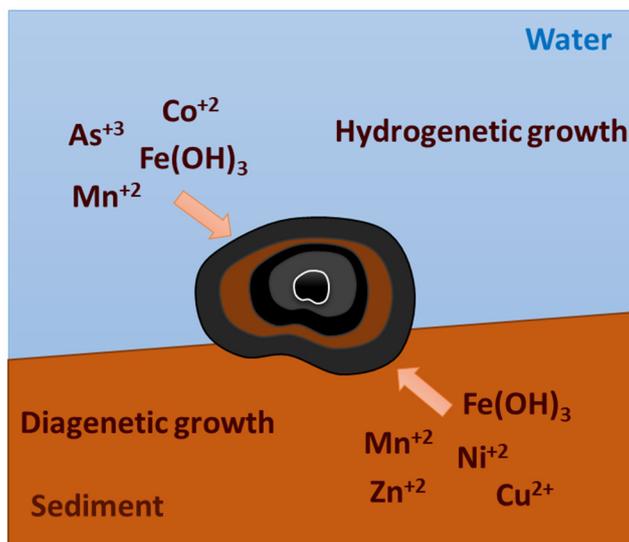
**Figure 1.** Manganese nodule collected in the Solwara 1 project (Source: [18]).

### 2.1. Formation and Growth

Manganese nodules are formed by the precipitation of Mn and Fe oxides around a nucleus formed by fossil remains such as shark teeth, basalt fragments, or the broken fragments of older previously formed nodules [19]. Mineral agglomerations can be classified into two groups. However, most nodules are believed to be an amalgam of both processes [20,21]:

- Hydrogenetic nodules are minerals accumulate by precipitation directly from seawater [15,16]. They are polynuclear and irregular, with smooth and finely porous textures, in which the predominant Mn mineral is vernadite ( $\delta$ -MnO<sub>2</sub>). This type of nodule is believed to have a similar content of Fe and Mn and a relatively high degree of nickel, copper, and cobalt.
- Diagenetic nodules are formed due to the precipitation of elements from interstitial water within the sediment or on the sediment surface [15,16]. They are commonly ellipsoidal to discoidal with porous and sandy surfaces, with Todorokite being the dominant mineral. Such nodules are rich in manganese but poor in Fe, Ni, Cu, and Co.

Natural deposits can indeed be formed by a combination of these two endmembers. Moreover, these processes concentrate the metals during their formation and growth throughout millions of years. Diagenetic processes can generate the mobility of fluid by pore water action; these fluids, enriched in metals (essentially Mn, Ni, and Cu), precipitate around a nucleus forming intrinsically with the Mn nodule itself. On the other hand, hydrogenetic precipitation is possible when nodule surface is exposed to seawater, in the presence of bottom currents strong enough to keep them clean of sediments; these types of nodules can have similar Fe and Mn content to diagenetic but usually have a higher Co content [22] (see Figure 2). However, hydrogenetic layers have less Ni and Cu than diagenetic [23].

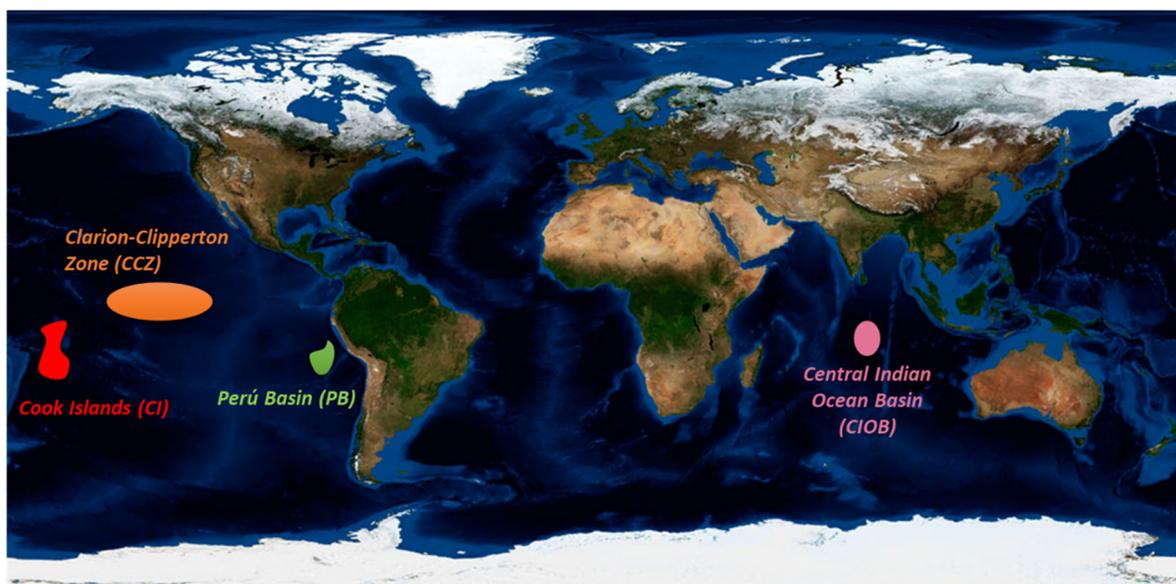


**Figure 2.** Types of growth of manganese nodules (modified from Marino et al. [24]).

### 2.2. Distribution in the World

Manganese nodules can be found in different types of environments, such as freshwater lakes, fjords, continental shelves, seamounts, plains, and abyssal basins [25]. The nodules are scattered at the sediment–water interface but are also found, mainly, at the water interface of the seabed and buried in the sediment [26].

Despite the fact that manganese nodules are scattered on most ocean floors, at depths greater than 4000 m, their local presence is sporadic. For example, the nodules can cover more than 75% of the sea floor or cover an almost null portion of a few hundred meters [27]. Figure 3 indicates the geographical location of the areas whose concentrations of manganese nodules are of real economic importance (rich in Mn, Ni, Cu, and Co); the areas are the Clarion-Clipperton Zone (CCZ), the Peru Basin (PB), the Central Indian Ocean Basin (CIOB), and the Cook Islands area [11,25].



**Figure 3.** Areas with deposits rich in manganese nodules (modified from Freepik [28]).

### 2.2.1. Clarion-Clipperton Zone (CCZ)

Located in the central Pacific Ocean, between Mexico and Hawaii, this region concentrates the largest number of continuous manganese nodule fields, with a total area of approximately four million square meters [29]. It is estimated that up to 10 billion tons of nodules can be recovered, from a total of approximately 21 billion tons, which is equivalent to six billion tons of manganese. The abundance of nodules in this area varies between 0 kg/m<sup>2</sup> and approximately 30 kg/m<sup>2</sup> [11,22]. These nodules are characterized by being a mixture of siliceous silt and deep sea clay [29].

The total manganese reserves present in the CCZ is equal to the world's terrestrial reserves of this metal. Meanwhile, the total tonnages of Ni, Co, Y, and Tl are higher than the terrestrial reserves, which is why the extraction of the manganese nodules has a significant effect on the production and the prices of these elements. Currently, there are nine bodies authorized by the International Seabed Authority for exploration in this area—China, Japan, the People's Republic of Korea, France, the Inter-Ocean Metal Joint Organization, the Russian Federation, Germany, Tonga Offshore Mining, and Nauru Ocean Resources [11].

### 2.2.2. Peru Basin (PB)

The Peru Basin is located in the Nazca Plate and is 3000 km off the coast of Peru, with an expansion equivalent to half of the CCZ. The depth of the water in the central part of the basin is approximately 4200 m, decreasing to 3950 m near the northern border [30]. In comparing the nodules of the Peru Basin with those located in the CCZ, lower contents of Cu and Co are observed. The amount of Ni and Mo are quite similar, but there is higher richness in Li in addition to Mn/Fe, which indicates that the PB deposits are older [2]. The nodules of the Peru Basin have a high carbonate content (up to 50%). Unlike CCZ, this is because most of these concretions are close to the depth of the calcite compensation [31].

In this area, the average concentration of manganese nodules is 10 kg/m<sup>2</sup> [11], but the concretions are different from one end to the other. In the south, small flat nodules appear with relatively smooth surfaces in amounts ranging from 6 kg/m<sup>2</sup> to 12 kg/m<sup>2</sup>. In the northern part, there are large, rounded nodules, which cover between 20 kg/m<sup>2</sup> to 30 kg/m<sup>2</sup> [32].

### 2.2.3. The Central Indian Ocean Basin (CIOB)

The polymetallic nodules of the Indian Ocean are distributed into the following four sectors: Crozet Basin, Wharton Basin, Somalia Basin, and the Central Basin, the latter being the most enriched [33]. It extends from Sri Lanka to the northeast slope of the mountain range that extends toward central India. It is delimited by the great linear submarine ridges Chagos Laccadive and Ninetyeast [34].

The nodule fields in CIOB occupy an area of 700,000 km<sup>2</sup>, and they are located at a depth of between 3000 m and 6000 m. Within the same area, there is a sector (300,000 km<sup>2</sup>) with the highest concentration of nodules called the Nodule Field of the Indian Ocean [35], with reserves reaching approximately 1.4 billion tons with an average abundance of 4.5 kg/m<sup>2</sup> [11]. The concretions of the Central Basin vary greatly between the different sectors. The manganese nodules of the southern region are formed by siliceous sediments, while for the north side, terrigenous and mixed terrigen-siliceous sediments predominate [36]. Due to sedimentation rates, the northern nodules are smaller than the southern ones, and in turn, studies reveal that the smaller concretions are richer in Mn, Cu, and Ni [37].

### 2.2.4. Cook Islands (CI)

The Cook Islands is an autonomous territory of the South-Central Pacific made up of 15 islands. The Exclusive Economic Zone (EEZ) of the CI has a total area of two million km<sup>2</sup>, where more than half are in deep water of up to 5500 m, which is rich in manganese nodules [38]. The area is characterized by low sedimentation rates, low organic matter flows, and an abundant supply of core material [39]. For the southern sector, there are sediments composed of ferrous-manganiferous clays of brown color, while in the north, these become more calcareous and siliceous [38].

It is estimated that this EEZ contains the most abundant fields in the world, reaching 7.4 trillion manganese nodules (20 billion tons of nodules), which stand out for having high cobalt content; almost 20% of the known Co resources in the world are found here [40]. Furthermore, they are all predominantly composed of  $\delta$ -MnO<sub>2</sub> and Fe oxyhydroxide [39].

The enriched fields in the Cook Islands have concentrations of manganese nodules ranging from 19 kg/m<sup>2</sup> to 45 kg/m<sup>2</sup> but reach maximums of up to 60 kg/m<sup>2</sup>. These concretions contain high amounts of cobalt (0.41%), titanium (1.20%), and yttrium (0.17%), but they are low in nickel (0.38%), copper (0.23%), and manganese (16.1%) compared to CCZ nodules [40].

### 2.2.5. Other Areas

In the depths of the Gulfs of Riga, Finland, and Bothnia, there are concentrations of nodules between 10 kg/m<sup>2</sup> and 40 kg/m<sup>2</sup>. The Gulf of Finland has reserves of six million tons of manganese nodules [11]. Notable work has also been done to explore and characterize Fe–Mn crusts near the Canary Islands [24,41,42], as well as Mn nodules near the Gulf of Cadiz [43–46] and in the Galicia Bank [47]; these deposits have been affected by the Mediterranean Outflow Water following the Late Messinian period, and are therefore interesting from paleoenvironmental and economic perspectives [46].

### 2.3. Chemical and Mineralogical Composition

The composition of manganese nodules depends on the genetic processes that contribute to their formation; hydrogenetic nodules, which have a lower Mn<sup>2+</sup> content than diagenetic, are dominated by Fe-vernadite, Mn-feroxyhyte, and busserite while diagenetic nodules are dominated by busserite, birnessite, and todorokite [13]. These two growth types—diagenetic and hydrogenetic—reflect suboxic and oxic growth, which in turn are related to periods of interglacial and glacial climate. It has been estimated that oxic-hydrogenetic type 1 layers make up about 35–40% of the chemical inventory of the CCZ nodules whereas suboxic-diagenetic type 2 layers comprise an even larger portion (50–60%). The remaining portion (5–10%) of the nodules consists of incorporated sediment particles that occur along cracks and pores [14].

The nodules are mainly composed of Mn oxides and Fe oxyhydroxides [11]. In turn, the Mn oxides minerals are decomposed into tectomanganates and phyllomanganates, both containing MnO<sub>6</sub> octahedral layers; the tectomanganate MnO<sub>6</sub> layers are organized into three-dimensional tunnel structures (e.g., todorokite), whereas the phyllomanganates MnO<sub>6</sub> layers are separated by hydrated interlayers that can be disordered (vernadite), ordered with a single plane of H<sub>2</sub>O molecules (birnessite) or ordered with two planes of H<sub>2</sub>O molecules (busserite). The todorokite, vernadite, birnessite, and busserite structures are each susceptible to isomorphic substitution of Mn<sup>4+</sup> within the MnO<sub>6</sub> layers, to host lower valence ions such as Mn<sup>3+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, or Co<sup>3+</sup>; as mentioned earlier, diagenetic growth favors exposure Ni<sup>2+</sup> and Cu<sup>2+</sup>, whereas hydrogenetic growth favors Co<sup>3+</sup> [23]. In addition to Mn<sup>4+</sup> substitution of the ions, there can also be Mn<sup>4+</sup> vacancies; in either case, the resulting charge deficits are compensated by inclusions within the interlayer or tunnel structure, hence the further incorporation of ions such as Mn<sup>2+</sup>, Mn<sup>3+</sup>, Na<sup>+</sup>, Li<sup>+</sup>, Ca<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup> and other ions [11,23,24]. Regarding Fe minerals, goethite (FeOOH), lepidocrocite ( $\gamma$ -Fe<sup>3+</sup>O(OH)) [45], ferroxhyte ( $\delta'$ -FeOOH) [48], and hematite (Fe<sub>2</sub>O<sub>3</sub>) [49,50] have been reported.

Manganese nodules have high concentrations of Mn, which are usually 3–6 times higher than Fe, unlike Fe–Mn crusts. Also, it is highlighted that manganese nodules are more enriched with Ni, Cu, and Li than the Fe–Mn crusts, with similar amounts of Mo, while crusts are more enriched with Co and rare earth elements [2]. These ferromanganese crusts are the result of precipitation, and consist of fine porous minerals that are dark coloured or black [24]. As seen in Table 1, the manganese nodules of the Peruvian basin usually have very high Mn concentrations, while in the Cook Islands, they have much lower concentrations (approximately half) [19].

**Table 1.** Chemical composition of manganese nodules for the different oceanic areas of the world (modified from Hein [19]).

Element	CCZ Nodules	Peru Basin Nodules	Indian Ocean Nodules	Cook Island Nodules
	Mean	Mean	Mean	Mean
Fe (wt.%)	6.16	6.12	7.14	16.1
Mn	28.4	34.2	24.4	15.9
Si	6.55	4.82	10.02	8.24
Al	2.36	1.5	2.92	3.25
Ti	0.32	0.16	0.42	1.15
Bi (ppm)	8.8	3.3	-	11
Co	2.098	475	1111	4116
Cu	10,704	5988	10,406	2290
Li	131	311	110	61
Mo	590	547	600	262
Nb	22	13	98	92
Ni	13,002	13,008	11,010	3756
Pb	338	121	731	2000
Pt	0.13	0.04	-	0.21
Te	3.6	1.7	40	23
Th	15	6.9	76	34
Tl	199	129	347	138
V	445	431	497	920
W	62	75	92	59
Zn	1366	1845	1207	516
Zr	307	325	752	468
REE	813	403	1039	1707

#### 2.4. Collection Mechanisms

All proposals for mining operations to extract minerals from the seabed are based on a similar concept of using a seabed resource collector, an elevation system, and support vessels for the processing and transportation of the mineral offshore; most of these systems provide for the use of vehicles to extract deposits from the seabed with mechanical drills or pressurized water, and they are controlled remotely [51].

There are three basic design concepts for manganese nodule extraction technology; lifting them with a dredge-type collector and lifting them through a pipeline (hydraulic mining system); collecting the nodules with tubular equipment, then pulling with ropes (continuous line bucket mining system); and nodule capture with a dredger-type collector, which ascends by the force of its own buoyancy (the modular mining system) [52].

A variety of mining technologies have been developed specifically for the extraction of polymetallic nodules, such as the examples presented below [11,53,54]:

- IKS Germany extracted manganese nodules using a collector mounted on a powered track; the extraction system includes a flexible hose for the hydraulic transport of solids with a high-pressure inlet. There is a satellite extraction system consisting of several small mining units and a mothership.
- DORD (Japan) tested recovering manganese nodules with a collector system supported by five sleds and equipped with four units of suction and intake devices between sledges.
- COMRA, in China, has worked on a special system to collect manganese nodules, and it is a hybrid collector based on hydraulic principles. It consists of a catchment device, double jets and deflector plates, a coanda nozzle and a transport channel, and an outlet with a grid to separate the sediments from the nodules. It is reported to have a high collection rate and low sediment content.
- KORDI, Korea, in order to collect the Mn nodules, developed a collection device consisting of a hydraulic lift and a mechanical conveyor. The detachment and separation of the nodules (from the sediments) is carried out by the joint action of a pair of water jets and deflector plates. A rotating fin system draws the nodules to the collector.

- Department of Ocean Development (India) extraction equipment consists of a crawler vehicle, a mechanical screw harvesting head, a bucket elevator to transport the nodule to the hopper, a crusher and a pump for transporting the mixture of nodules and water to the vertical module. Once the nodules are tracked, the screw transports (from the collector head) sweep the material of interest dispersed to the elevator, pass to the hopper where they are crushed (to 10 mm), and they finally reach the vertical module.
- Atlantis Deep Sea, in the USA, developed a nodule recovery kit that has two parts—A surface subsystem and an ocean floor subsystem. The upper part includes a ship for operational control and maintenance support for the lower subsystem. The ocean floor subsystem has a mobile, maneuverable, and self-propelled mining vehicle that collects, handles, washes, and crushes nodules. It includes a shock absorber that temporarily stores the crushed material and serves to isolate the mining vehicle from the dynamics of a pipe that extends downward from the surface of the ship. The global system has sensors that detect the location of the mining vehicle and show the topography of the ocean floor where it is applied.

It is important to highlight that profitable exploitation of deep-sea mining is only feasible with the premise that there is a nodule collector with a maximum collection capacity of 140 kg of wet nodules per second. In addition to collection efficiency, mining processes that are less damaging and polluting are also required because deep sea mining could be a new environmental challenge related to ocean biology [54].

### 2.5. Resource Quantification

A high level of confidence in resource data is a key prerequisite for conducting a reliable economic feasibility study in deep water seafloor mining. However, the acquisition of accurate resource data is difficult when employing traditional point-sampling methods to assess the resource potential of manganese nodules, given the vast size of the survey area and high spatial variability in nodule distribution. A challenge for resource geologists is that the composition of nodules is not uniform. Research has shown that deposits found only several 100 m apart can vary appreciably in composition—the concentration of minerals in nodules found in the North Pacific belt appears to be greater than the South Pacific; percentage values from the former region are reported as 22–27% Mn; 1.2–1.4% Ni; 0.9–1.1% Cu; 0.15–0.25% Co; 5–9% Fe [55]. There are undoubtedly site-specific aspects that would override the implications of ocean-scale sampling; as previously discussed, the combination of hydrogenetic and diagenetic processes determine the prevalence of Ni and Cu, versus Co [23,24], and can indeed be site-specific.

## 3. Manganese Nodules in Chile

Chile has a total Exclusive Economic Zone of 4,264,560 km<sup>2</sup> containing a variety of marine resources [12,56], where there are potential minerals and areas of great economic interest, in which manganese nodules can be found, as well as ferromanganese crusts and submarine polymetallic sulphides (see Figure 4). According to the bathymetric, geological, geophysical, and geochemical information from the Chilean EEZ, the main underwater resources are detailed below:

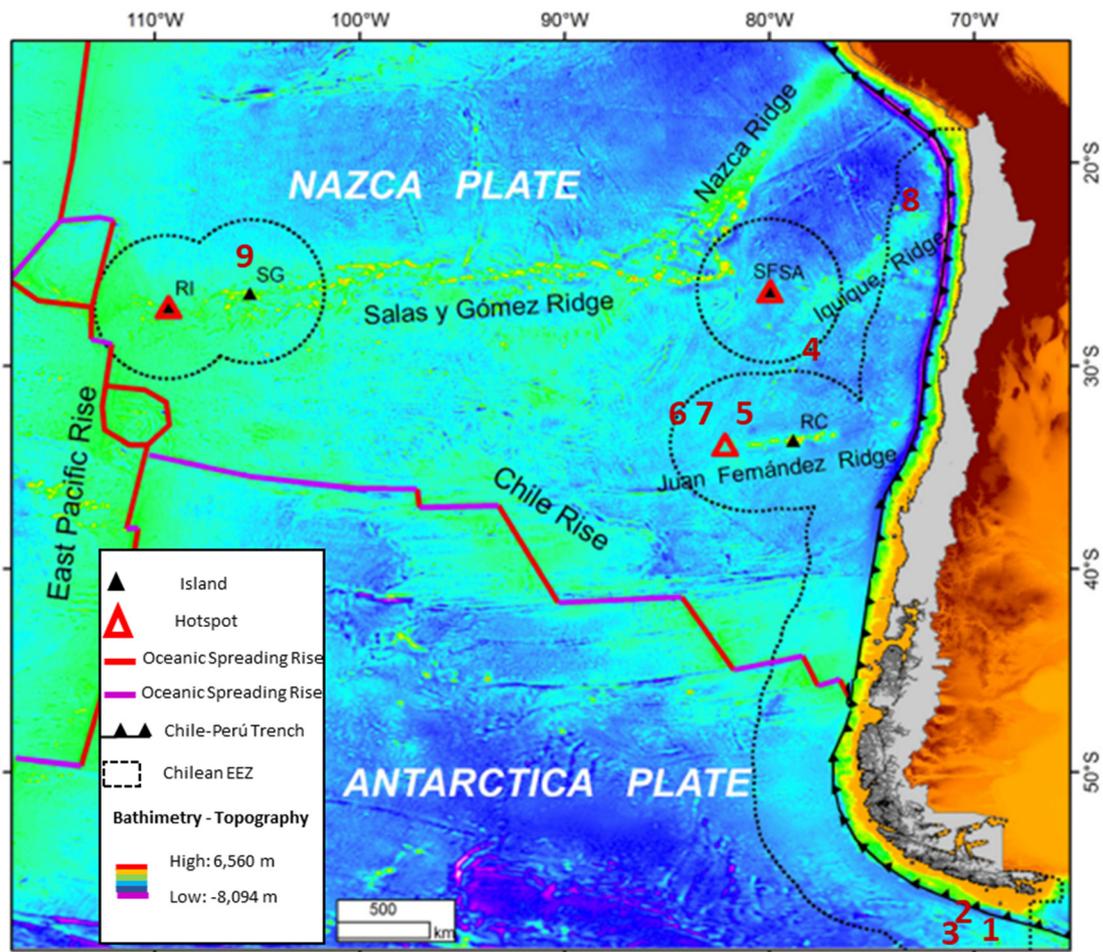
- Manganese nodules—the known reserves within Chile are as follows: Robinson Crusoe Island, at 3820 m depth, with a nodule concentration of 4–5 kg/m<sup>2</sup>, with a combined Ni + Co + Cu grade of 0.87%. At the mouth of the Rio Loa, 4332 m deep, there are fields with a Cu + Ni content of 1.38% (Site 7 of Table 2). Surrounding the Juan Fernandez ridge there is a zone of manganese nodules that is between 3650 m and 3873 m deep, having a combined Cu + Ni grade between 0.25% and 0.96%. Surrounding the San Francisco and San Antonio Islands, grades of up to 19.8% Fe, 14.638% Mn, and 0.305% Co have been observed (Site 4 of Table 2). In Northern Chile, at a depth of 4332 m, nodules have been sampled which contain an average of 0.65% Cu, 0.73% Ni and 0.81% Zn (Site 8 of Table 2). Close to the Salas and Gomez Islands, at a depth of 2890 m, nodule samples having an

Fe grade of 18.8% and combined Cu+Ni grades of 0.6% have been collected (Site 9 of Table 2). In Southern Chile, south of the Magallanes, samples have been collected at depths ranging from 3767 m to 4007 m, with Mn grades that vary between 7.993% and 16.63%, Cu + Ni grades between 0.3% and 0.57%, and Co grades between 0.163% and 0.532% (Sites 1, 2, and 3 of Table 2) [12,14,57]

- Ferromanganese crusts—within the Chilean territory, the most promising area regarding ferromanganese crusts is found in the volcanic cord of which the Salas and Gómez and San Félix and San Ambrosio islands are part, as are the sedimentary basins that surround the Island Easter. The metallic content in these areas is relatively low in terms of copper and nickel concentration (between 0.25% and 0.30%), but it has a significant manganese content (10%) [12,14].
- Submarine polymetallic sulphides—To date, no deposit of massive sulphides from the seabed in Chile has been systematically sampled. However, the German Geometep program did explorations in the Eastern Pacific Ridge, to the north and south of Easter Island, where black chimneys and smokers were photographed and sampled at high temperatures at a depth of 2550 m. Based on the studies carried out in this exploration, it was estimated that these deposits could contain 300–500 g/t silver, 5–10 g/t gold, 10–20% zinc, 5–10% lead, and 1–10% copper [12,58].
- Sediments—in the national territory, there are sediments with a significant amount of marine phosphorites ( $P_2O_5$ ), where the two main deposits are found on the Mejillones Peninsula, where it is estimated that the average phosphate grade is between 6% and 7%, and the Caldera Basin with an average grade of 18% of  $P_2O_5$  [12,14]. Also, there are submarine gas hydrates, where there is a huge natural gas field (7500 km<sup>2</sup>), just 50 km from the Chilean coast, which extends from the city of Valparaíso to Puerto Montt [59,60].

**Table 2.** Location, depth, and chemical analysis of manganese nodules within diverse marine regions surrounding Chile (labeled as numbers 1–9 in Figure 5). (Adapted from García et al. [61].)

Location	Nodule Sample								
	1	2	3	4	5	6	7	8	9
Latitude S	59.017	57.983	57.083	30.392	33.05	33.042	33.033	21.338	26.2
Longitude W	70.75	70.883	70.983	78.98	82.05	83.942	84.05	73.908	106.3
Depth (m)	3797	4007	3767	3820	3881	3650	3873	4332	2890
Element (wt.%)									
Fe	24.56	17.957	18.02	19.802	16.375	19.25	6.7	6.7	18.8
Mn	16.63	15.183	7.993	14.638	17.067	-	10.1	10.1	10.6
Ni	0.2	0.435	0.357	0.295	0.518	0.285	0.5	0.73	0.43
Cu	0.1	0.135	0.153	0.238	0.3	0.175	0.23	0.65	0.17
Co	0.24	0.532	0.163	0.305	0.108	0.105	0.14	0.04	0.14
Zn	0.07	0.084	0.068	0.052	0.08	0.065	0.07	0.81	-
Pb	0.28	0.11	0.07	0.1	-	-	0.06	0.03	-
Mo	-	-	-	0.026	-	0.048	-	-	-
Cu + Ni	0.3	0.57	0.51	0.533	0.818	0.46	0.73	1.38	0.6



**Figure 4.** Islands with potential mineral resources to be exploited in the Chilean EEZ. RC: Robinson Crusoe Osland; SF: San Félix Island; SA: San Ambrosio Island; RI: Rapanui Island; SG: Salas y Gómez Osland; AS: Alejandro Selkirk Island (adapted from García et al. [61]).

### 3.1. Exploitation of Submarine Deposits in Chile

The greatest challenge in the extraction of maritime resources in Chile will be the protection of the delicate ecosystems. Accordingly, concern has been brought forth by environmental groups that seek to protect the marine flora and fauna.

The regulations and measures that specify the rights to marine resources in Chile and contain laws for mining development are described in Consejo Minero [62]:

- Decree Law No. 3525/1980: National Service of Geology and Mining;
- Law No. 18.097/1982: Organic Constitutional Law on Mining Concessions;
- Law No. 18,248/1983: Mining Code;
- Decree No. 1/1987: Mining Code Regulations;
- Decree with Force of Law No. 1/1987: Creation of the Chilean Copper Commission;
- Decree No. 132/2004: Mining Safety Regulations;
- Law No. 20,551/2011: Closure of Mining Works and Installations;
- Decree No. 41/2012: Regulation Closing Works and Mining Facilities;
- Decree No. 100/2013: Creation of the International Mining Advisory Council.

### 3.2. Challenges to the Exploration and Exploitation of Manganese Nodules

Different consortiums have developed techniques to locate, quantify, and assess the most viable nodule deposits in the Pacific. The exploration is done using ships that are equipped with an array of devices that collect samples with precision geolocation, photographing the ocean floor, performing precision bathymetry, and complemented by chemical analysis [11]. The technology used for deep-sea exploration of Mn nodules includes high-resolution seismic reflectometry, electron probe microanalysis (EPMA), X-ray diffraction (XRD), X-ray fluorescence (XRF), gas chromatography, and inductively coupled plasma (ICP) mass spectrometry [41,46]. In particular, strontium isotope analysis ( $^{87}\text{Sr}/^{86}\text{Sr}$ ) is applied over the cross-section of the nodules to gain insight into their growth history, including the possible influence of radiogenic fluids [44,46]. Analysis of thorium isotopes ( $^{230}\text{Th}_{\text{excess}}/^{232}\text{Th}$ ) can be combined with ICP to determine the growth rate and age [46].

Despite the long history of deep-water exploration (since the early 19th century), it continues to present technological challenges even into modern times. The main challenges for large-scale mining operations include the following considerations [11]:

- The duration of commercial mining operations is long;
- It is difficult to predict the climatic changes over a sufficiently long timeframe;
- There is a lack of data, and examples of large-scale operations to serve as benchmarks;
- It is difficult for equipment to be well maintained over time, especially in systems that are under such extreme hydrostatic pressure.

The Chilean deposits have considerable economic potential, yet they have not been explored to a satisfactory level, possibly due to the available opportunities for conventional land-based mining within Chile [61]. The CCZ, PB, CIOB, and CI deposits have been characterized to a far greater extent than the those of Chile [11]. There is a far better understanding of the geological setting surrounding the Gulf of Cadiz [43–46] and in the Galicia Bank [47], considering the effect of the Mediterranean outflow water undercurrent [45], the type of sediments, limits of the basis, volcanism, etc. The studies made for these other regions are a benchmark for future initiatives within the Chilean EEZ.

### 3.3. Environmental Issues

Seabed mining generates long-term impacts that require long recuperation times, including physical impact on the ocean floor, particle suspension, trophic alteration, etc. Regarding manganese nodules, their formation is the result of millions of years of mineral precipitation surrounding objects such as fish teeth, bones, etc. Thus, these resources are clearly non-renewable from any practical standpoint [63].

Far more critical, however, is the impact on the benthonic habitats, and it is not yet known exactly how rapidly it could be replenished. Studies have revealed the vast diversity of lifeforms that live on the sediments that host the manganese nodules, and within the overlying strata of oceanwater; diverse species of worms, crustaceans, sea cucumbers, star fish, and a plethora of protozoa [63]. A particular study began in 1978 investigating the potential environmental damage that would be caused by the extraction of manganese nodules; even after 26 years, the disturbances caused by the submarine vehicles remain visible, and the biomass of nematode worms is significantly lower than the surrounding undisturbed areas [63].

### 3.4. Context of the Manganese and Cobalt Market in Chile

Chilean manganese production began in the 19th century. This occurred as a consequence of the high international demand for the increasing use of ferromanganese in the Bessemer steel process. In the first 10 years, Chile reached annual productions of 52,000 tons of Mn, which were exported to England. Subsequently, due to the drop in the price of this commodity, there was a significant decrease in production levels in the country. Due to the First and Second World Wars, there was a rebound in

Chilean manganese production, where production reached figures of 114,000 tons per year in 1943, and later, this production fell dramatically in 1945 [63].

Manganese production in Chile has been mainly for use in steel alloys, and it was relatively stable until 2009. After this date, only minor production exists, since the main companies that produce manganese within the country are currently in the process of closure [63,64]. According to internal reports from Chilean government entities, manganese production fell from 62,887 t per year in 1996 to 5722 t per year in 2009 (See Figure 5).

Regarding cobalt, the literature and historical records in Chile indicate that exploitation began in the country began in 1844, in the middle of the 19th century, and this commodity was exported and mainly used for its use in steel alloys. Although deposits with primary ore have been exploited for cobalt, the greatest occurrence and exploitation was cobalt along with copper. As in the manganese industry, the highest cobalt production in Chile occurred during World War II (20,000 t/year). Post-war, the demand for Co gradually decreased, and consequently, the mining companies dedicated to the exploitation and production of this element were closed, a situation that continues to this day [63]. There is interest on the part of investors to reactivate the exploitation of cobalt from these old abandoned mines [65]. However, although in those years, Chile operated with grades of 7.3%, better than the current 3% in the Congo, it is not known if the Chilean deposits constitute a viable mining sector under current conditions [4].

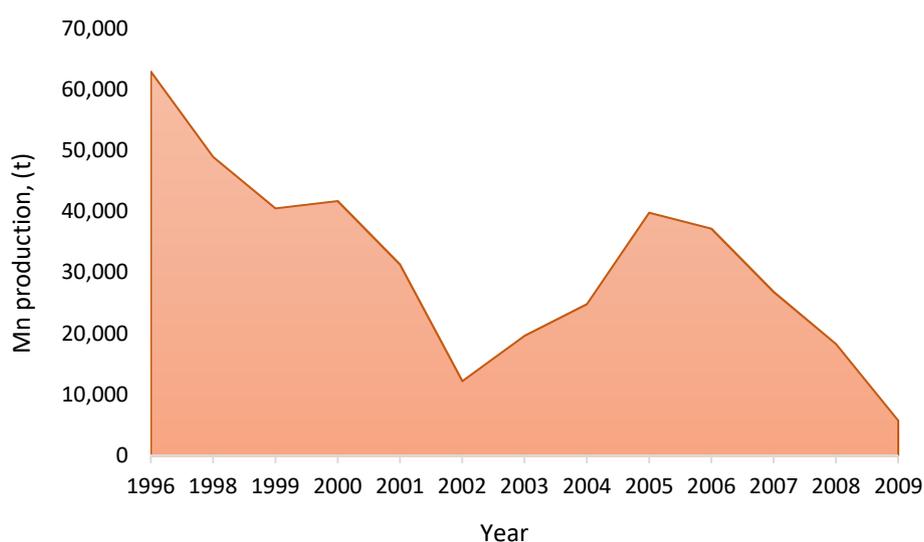


Figure 5. Historical production of Manganese in Chile (data from Cochilco [66]).

#### 4. Co and Mn Extractive Metallurgical Processes from Manganese Nodules

During recent decades, there have been a great deal of research and development on the extraction of these nodules from the seabed, which is basically due to the fact that land resources are being depleted. The amorphous composition of the nodules makes the extraction treatments of the elements of interest, and the presence of metals in the form of oxides and hydroxides, particularly complex and difficult [67]. Within manganese nodules, elements such as copper, nickel, and cobalt are found in the form of oxides in the Fe and manganese mineral networks. For the effective extraction of metals, it is necessary to break these networks. There are two categories of processing [68,69]:

- Pyro-hydrometallurgical method for processing manganese nodules. This technology has a pyrometallurgical stage that allows the selective reduction of non-ferrous metals. A polymetallic alloy (Fe-Cu-Ni-Co-Mn) and a SiMn slag are formed. Subsequently, the complex alloy goes into a hydrometallurgical stage.
- Hydrometallurgical method of selective dissolution or by autoclaving of manganese nodules. They are based on leaching in an acidic or alkaline medium with or without the presence of

reducing agents. In the case of the autoclave method, the process is exposed to a medium under high pressure and temperature.

Regarding these treatment routes, the humidity of the mineral is a very important consideration. An outstanding feature of manganese nodules is their high-water content held tenaciously, even at high temperatures, due to capillary condensation in extremely fine pores [70]. This water causes the pyrometallurgical stages to require a high energy consumption, making the hydrometallurgical route more likely to be used.

#### 4.1. Pyro-Hydrometallurgical Treatments

##### 4.1.1. Segregation by Roasting in the Presence of Chlorination Agents

In this process, segregation is carried out through roasting, where sodium chloride is added as a chlorination agent [71], which forms complexes with the transition metals (Ni, Cu, and Co) from the manganese nodules in a process at which the maximum solubility of metals is achieved at 700 °C and 850 °C [72]. Common chlorination agents are NaCl, MgCl<sub>2</sub>, NH<sub>4</sub>Cl, LiCl, CaCl<sub>2</sub>, and CsCl, and then leaching is performed using petroleum coke as a reductant.

The best conditions for metal segregation were achieved with CaCl<sub>2</sub> as the chloride source and with an operating time of 2 h. At 850 °C, the highest recovery of Copper was reached, 75%, but for nickel and cobalt, it did not exceed 25%. On the other hand, when the furnace works at temperatures of 1050 °C, the recovery of Cu reaches only 35%, while Ni and Mo reach 60%. The results revealed that the susceptibility of the metal segregation response follows the order Cu > Ni > Co > Fe > Mn [73].

##### 4.1.2. Metal Extraction by Sulfating Roasting and Leaching

The marine manganese nodules processed through sulfating roasting are carried in a reactor at temperatures from 100 °C to 1000 °C within a sulfating environment of SO<sub>2</sub>, followed by an aqueous leaching step [74].

Metallic forms of Mn, Ni, Co, and Cu can be selectively extracted from manganese nodules through ammonia leaching in which recovery of approximately 90% Mn, 90% Co, 70% Ni, 70% Cu, and 10% Fe is achieved [75,76]. Other antecedents indicate that when sulphating at 400 °C and subsequently leaching with boiling water, extraction of Ni, Cu, and Co can surpass 80% [77].

##### 4.1.3. Reduction of Manganese Nodules and Selective Ammonia Leaching

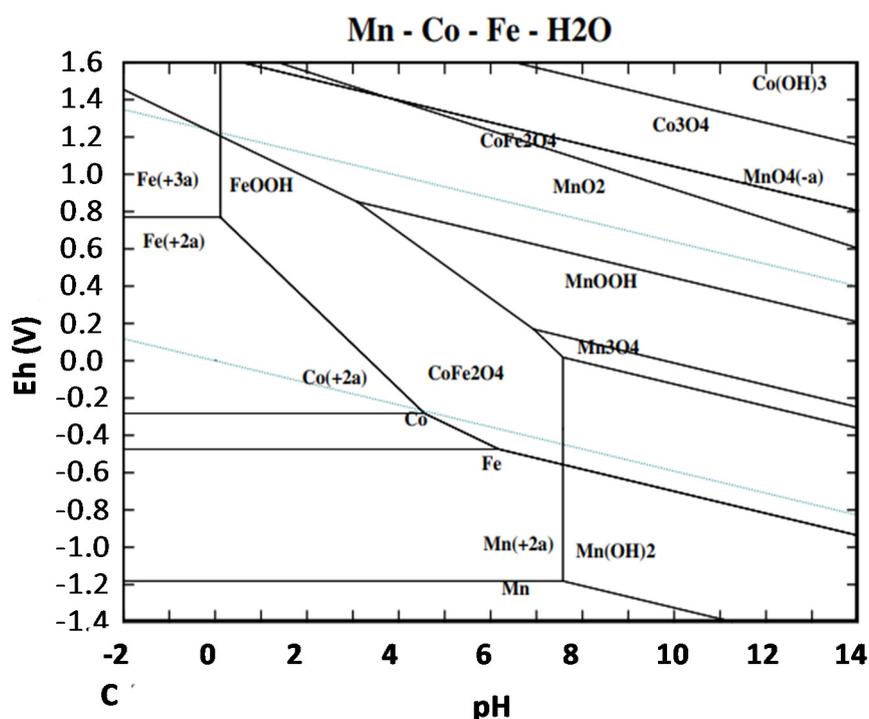
A third pyro-hydrometallurgical process to achieve the recovery of valuable metals from the manganese nodules is to selectively extract copper and nickel by initiating reduction in the presence of carbon or coke in an oven at 800 °C [78]. This is followed by a leaching process at room temperature to recover the copper present in the mineral; this is followed by a stage of leaching with ammonium salt at 50 °C, which allows the recovery of nickel. This approach achieves typical recoveries of 90% for Cu and 50% for Ni [77].

The composition of the manganese nodules has an observed effect on the reduction–ammonia leaching system of copper, nickel, and cobalt. After the roasting step, the manganese nodules (Ni, Cu, Co, Fe, and Mn) are leached using metallic powders in the ammonia–ammonium carbonate solutions. When manganese was added, the leaching of the other metals is affected, while Fe had no effect on the process [79].

#### 4.2. Hydrometallurgical Treatments

The dissolution of Mn from manganese nodules is a leaching process that works at low potential values. In order to extract manganese and other metals of interest from manganese nodules, the use of a reducing agent is necessary [68]. Work was reported with the use of different reducing agents, such as carbon [80], H<sub>2</sub>SO<sub>3</sub> [81,82], methanol [83], organic acids [84,85], sulfur dioxide [86], and various

Fe-containing reducing agents [87]. From the various reducing agents mentioned, Fe has presented better dissolution kinetics compared to the rest, and it also has the advantage of being an abundant and low-cost resource. Various studies were carried out to evaluate the effect of Fe as a reducing agent in acid leaching of marine nodule media [14,17,49,87,88]. For studies in acidic media and Fe, it was reported that the best results to extract manganese are obtained by increasing the amounts of Fe in the Mn/Fe ratio while working at low acid concentrations [49,88]. Figure 6 shows diagrams of the pH-potential at room temperature for the dissolution of Mn, Co, and Ni using Fe as a reducing agent.



**Figure 6.** Potential pH diagram for the Mn-Co-Fe-H<sub>2</sub>O system at 25 °C and unit activity (based on HSC 6.1; dashed lines represent O<sub>2</sub>/H<sub>2</sub>O and H<sub>2</sub>O/H<sub>2</sub> couples). (Adapted from Senanayake [89].)

As seen in Figure 1, with the dissolution of Mn and Co from manganese nodules at room temperature, the use of a reducing agent (in this case Fe) is necessary. The dissolution of both elements can be achieved in values of potential and pH between  $-0.2$  V to  $0.8$  V and  $-2$  to  $4.5$ . In addition, this leaching-reducing process is quite fast (processing times from 10 min to 30 min) when working in high concentrations of reducing agent, achieving extractions of both elements above 70%. The solid residues generated do not cause Fe precipitates, nor high toxicity, even when working with highly reactive compounds such as tailings [17].

#### 4.3. Tailings

An attractive feature of manganese nodules is that they are almost 100% composed of marketable materials, as opposed to terrestrial ores that often yield less than 1% marketable material; this considers that Mn alloying agents are directly sold to the steel industry in the form of ferromanganese [90]. Indeed, the processing of nodules may result in lower portions of solid waste in comparison to conventional mining by perhaps two orders of magnitude. Moreover, the treatment of these nodules does not result in the large volumes of sulfur-rich tailings, which are highly acidic and would need to be neutralized [17].

## 5. Conclusions

There is an increasing demand for various mineral resources by modern society and industries, in addition to the gradual depletion of resources in the Earth's crust. For this reason, research and development of the mineral resources of the seabed are increasingly attractive. Among marine minerals, manganese nodules have attracted an ever-increasing level of attention worldwide due to their high economic value and their relatively easy prospecting compared to other deep-sea resources.

Currently, large deposits of cobalt and manganese are not being exploited in Chile, mainly due to the apparent shortage of high-grade deposits of both elements. In the past, the fluctuation and decrease in the prices of these commodities has also had an influence. However, today, due to the rise in the price of cobalt, alternatives are being evaluated to enable large-scale production of this element. Given this scenario, manganese nodules are presented as a possible alternative for the country due to their high average Co and Mn grades, which in turn would allow the growth of strategic industries of value-added products including lithium batteries.

Chile's current environmental regulations prevent the exploitation of underwater resources. Even with the considerable gaps in geophysical, mineralogical, and environmental information that would support nodule exploitation in the Chilean EEZ (in comparison to the Gulf of Cadiz [43–46], for example), Chile is nonetheless the Latin American country that has the most information regarding its seabed. Moreover, the recent worldwide advances for the exploitation of large submarine mining are considerable. Therefore, the growth needs of the local industry and the search to create value-added products that could indeed allow Chile to compete with developed countries, which motivates the consideration of local manganese nodule excavation. However, despite all these positive comments regarding submarine mining, considerable damage would be generated to the marine ecosystem, which continues to raise doubts as to whether it is positive to exploit the country's seabed.

Among the treatment processes for manganese nodules for Co and Mn extraction, acid-reducing leaching processes for minerals with high MnO<sub>2</sub> content are presented as the apparent best alternative, compared to the traditional process that involves reduction at high temperatures from acid leaching. This is mainly due to its high Mn extraction and fast dissolution kinetics and also because it is a more environmentally friendly process, which meets the future standards of the low-carbon economy.

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