

Article



Research on Recovery of Valuable Metals from Cobalt-Rich Crust Using Carbon as a Reduction Agent during the Acid Baking Process

Da Li, Xunxiong Jiang *, Shengdong Wang, Xudong Sun, Feng Zhao 🔍, Linyong Feng and Denggao Zhang

BGRIMM Technology Group, Beijing 102600, China

* Correspondence: jiang_xx@bgrimm.com

Abstract: Cobalt-rich crust is a seabed metal mineral resource that is different from oceanic polymetallic nodules. Based on the higher Co content than polymetallic nodules, the commercial value of cobalt-rich crust may be better than that of polymetallic nodules. Due to the special distribution of valuable metals, commercial implementation is always limited. Herein, a novel process is proposed to efficiently and, in an eco-friendly way, recycle valuable metals from cobalt-rich crust. The results indicate that carbon could promote the decomposition of manganite in the cobalt-rich crust during the acid baking process, and the leaching ratio of Mn could increase by 50% when carbon is added during acid baking. In addition, it can be found that the promotion of carbon for Co is stronger at low sulfuric acid consumption than that at high sulfuric acid consumption; however, there is no promotion of carbon for leaching Ni and Cu during the acid baking process. The leaching ratio of Ni, Co, Cu, Mn, and Fe reached 98.59%, 91.62%, 93.81%, 41.27%, and 26.94%, respectively, when the mass ratio of the sulfuric acid and cobalt-rich crust was 0.567, the mass ratio of the carbon and cobalt-rich crust was 0.1, the temperature was 200 °C and the time was 240 min. This research could provide an alternative economic process for recycling valuable metals from cobalt-rich crusts.

Keywords: cobalt-rich crust; cobalt; nickel; manganese

1. Introduction

Cobalt and cobalt oxides are extensively used in a wide range of industrial and military applications such as superalloys, catalysts, cemented carbide, and lithium-ion batteries [1]. With the rapid growth in electric vehicle use in recent years, the growth of lithium battery use, driven by electric vehicles, promotes the demand for cobalt. According to the demand data of cobalt in all the applied fields, consumption of cobalt in lithiumion batteries accounted for 49% of total cobalt consumption in 2015; it is estimated that the consumption of cobalt in lithium-ion batteries will increase to 80% in 2030. It is estimated by the IEA 2DS (International Energy Agency 2-Degree Scenario) and IEA B2DS (International Energy Agency Below 2-Degree Scenario) that the annual cobalt demand will reach 300,000–400,000 tons in 2030 [2]. According to survey data published by the USGS (United States Geological Survey) in 2021, the world cobalt mine reserves are about 7.1 million tons. However, more than 120 million tons of cobalt resources have been identified in manganese nodules and crusts on the floor of the Atlantic, Indian, and Pacific Oceans and the cobalt resources in the ocean are 4.8 times more than that on land [3]. Due to the increase in demand for cobalt coupled with the depletion of land-based high-grade ores, ocean resources containing cobalt are being viewed as a future potential resource [4].

In the 1980s, some researchers drew attention to the cobalt-rich crusts and pointed out that the areas of cobalt-rich crust were centered mainly in the western and southern Pacific [5–7]. In the same era, the cooperative sea-floor research organization of Germany and the U.S discovered cobalt-rich crust at sea mounts of the Central Pacific Ocean [8]. Due to higher cobalt content in the cobalt-rich crust than in ferromanganese nodules, research



Citation: Li, D.; Jiang, X.; Wang, S.; Sun, X.; Zhao, F.; Feng, L.; Zhang, D. Research on Recovery of Valuable Metals from Cobalt-Rich Crust Using Carbon as a Reduction Agent during the Acid Baking Process. *Minerals* 2022, *12*, 1215. https://doi.org/ 10.3390/min12101215

Academic Editors: Tetsuo Yamazaki and Sup Hong

Received: 1 August 2022 Accepted: 20 September 2022 Published: 26 September 2022

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2022 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/). on cobalt-rich crusts as a potential and strategic substitute for cobalt mines on land gained prominence in the early 1980s [9,10]. Until recent years, the cobalt-rich crust is still seen as an additional source of raw materials besides land-based sources [11]. Up to now, several studies have been investigated to concentrate and recover Co and Ni from cobalt-rich crust including mineral processing [12], pyrometallurgy [13–18], and hydrometallurgy [19–23]. Because of the high-water content in cobalt-rich crust, hydrometallurgy may be a good choice for the recovery of Co and Ni. Due to the high content of Mn and Fe in the cobaltrich crust, the reductive ammonia leaching process is preferred to recover Co and Ni selectively. However, the ammonia-nitrogen wastewater discharged from the reductive ammonia leaching technique limits the industrial application of this technique [24–26]. Due to the inevitable environmental problem caused by the ammonia leaching process, the reductive acid leaching process of the cobalt-rich crust could be a good choice for the recovery of Co and Ni. The hydrochloric acid and nitric acid leaching techniques are not suitable for practical application for the cobalt-rich crust because of the high price of hydrochloric acid and nitric acid. The reductive sulfuric acid leaching technique is an appropriate approach for treating cobalt-rich crust. To eliminate the effects of impurities brought by the reduction agent in the sulfuric acid leaching technique, SO_2 and H_2O_2 were used as reduction agents in the sulfuric acid leaching process [27,28]. However, the high-cost problem of SO₂ and H₂O₂ always ailed the industrial application of the reductive sulfuric acid leaching technique.

The aim of this study was to solve the high-cost problem of reduction agents in traditional sulfuric acid leaching techniques and use carbon as the reduction agent to reduce the high valence Mn in the cobalt-rich crust acid baking process. Then, the Co and Ni which were associated with Mn-oxides in the crust are released to the aqueous phase concurrent with the dissolution of low valence Mn reduced. Finally, the Co, Ni, and a part of Mn could be recovered from the leaching solution. Compared with other sulfuric acid leaching technologies, our proposed sulfuric acid baking technique could make full use of the heat of reactions between sulfuric acid and oxides in the cobalt-rich crust. In addition, the cheaper anthracite used as the reducing agent in acid baking replaced the more expensive H_2O_2 and SO_2 . Therefore, the cost of our technology based on such advantages might be lower than other sulfuric acid leaching techniques. Ultimately, this research provided a Co and Ni recovery process from the cobalt-rich crust by using carbon as the reduction agent in the acid baking process, which might not only solve the reproduction of the reduction agent but also be industrialized easily.

2. Materials and Methods

2.1. Materials

The cobalt-rich crust samples were obtained from the China Ocean Sample Repository (COSR), Qingdao, China. The fine crust samples were crushed and ground finely (more than 80% particle size < 75 μ m), and the raw materials were dried at 80 °C in a vacuum dryer for 12 h before subsequent experiments.

2.2. Experiments

The details of the acid baking process are presented as follows: The 30 g fine cobalt-rich crusts and sulfuric acid (98 wt%) with different acid/crust mass ratios (A/C ratio) were homogeneously mixed. The mixtures were roasted for 240 min at different temperatures by using a muffle furnace (KSXQ-16-12, Yixing Sunnorn Furnace Co., Ltd., Yixing, China) with a temperature control accuracy of ± 2 °C. After naturally cooling to room temperature, the baking product was used as the experimental material for the subsequent leaching process.

The details of the leaching process are presented as follows: The baking products were leached under the conditions of leaching temperature of 90 °C, leaching time of 60 min, and solid/liquid (g/mL) of 1/4. The schematic of the experimental process is shown in Figure 1. At the end of each leaching test, the residues were separated from the leachate by vacuum filtration and were later washed using hot deionized water (80–90 °C) until

the pH of the last filtrate was approximate 7. After drying at 100 $^{\circ}$ C for 24 h, the leaching residues were analyzed by ICP-OES for chemical composition and by XRD, and SEM for phase composition. The metals extraction efficiency of cobalt-rich crusts was calculated using Equation (1):

$$R_M = \left[1 - \frac{w_0 \times M_0 - w_1 \times M_1}{w_0 \times M_0}\right] \times 100\%$$
(1)

where R_M is the leaching ratio of metals (Ni, Co, Cu, Mn, and Fe); w_0 or w_1 is the weight percentage of metals in the cobalt-rich crust or leaching residue; M_0 or M_1 is the weight of the cobalt-rich crust or leaching residue.



Figure 1. Schematic of acid baking of cobalt-rich crust.

2.3. Analysis Methods

The chemical composition of the cobalt-rich crusts, acid baking products, and leaching residues was determined by an inductively coupled plasma optical emission spectrometer (ICP-OES, Agilent 700, Agilent Technologies, Inc., Santa Clara, CA, USA). The high frequency-infrared carbon-sulfur spectrometry (HF-100, CS-344, LECO Corporation, St Joseph, MI, USA) was used to determine the contents of sulfur and carbon. The phase compositions of the cobalt-rich crusts and leaching residues were analyzed by an X-ray diffractometer (XRD, PANalytical Empyrean, Malvern Panalytical, Malvern, Worcs, UK) which was performed using Cu-K α X-radiation at a scan rate of 10° 2 θ /min. Morphological and chemical analyses of samples were performed via scanning electron microscopy (SEM, QUANTA 600, FEI Company, Hillsboro, OR, USA) with energy dispersive spectroscopy (EDS, EDAX genesis 7000, EDAX Inc., Mahwah, NJ, USA). The gas components of the gas exhausted during the acid baking process were analyzed by a gas analyzer (Gasmet Portable FT-IR Gas Analyzer; GASMET DX4000, Gasmet Technologies, Helsinki, Finland). The gas flow of N₂ as the carrier gas during the gas analysis process was 3L/min, and the gas components of gas were analyzed every 5 s.

3. Results

3.1. Characteristics of Cobalt-Rich Crust

The chemical composition of the cobalt-rich crust is presented in Table 1. As shown, the main elements of cobalt-rich crust are Mn and Fe.

Mn	Fe	Ni	Со	Cu	Мо	REES	Ti
20.17	16.18	0.41	0.54	0.11	0.051	0.1523	0.83
CaO	MgO	P_2O_5	Al_2O_3	Te,g/t	S	С	Pt,g/t
4.04	1.59	0.99	1.57	54	0.20	3.3	0.2283

Table 1. The chemical composition of cobalt-rich crust (wt%).

Figure 2 shows the XRD pattern of cobalt-rich crust. The diffraction peaks of goethite/ manganite (FeO(OH)/MnO(OH)) (FeO(OH):PDF#81-0464; MnO(OH):PDF#88-0649) and quartz (SiO₂) (PDF#05-0490) can be observed. However, the X-ray diffraction intensity of goethite/manganite is broad, which probably indicates that most goethite/manganite have poor crystallinity. However, there are some previous studies reporting that the manganite in the cobalt-rich crust was amorphous [29].



Figure 2. XRD pattern of the cobalt-rich crust.

Figure 3 displays the mapping scanning images of cobalt-rich crust and the EDS results shows the elemental composition of the red box area corresponding to SEM. We could find easily that the elements of Co, Mn, Fe, Ni, and O distribute uniformly in the cobalt-rich crust and the main elements in the cobalt-rich crust are Mn, Fe, and O.



Figure 3. Distribution of different elements in cobalt-rich crust. (a) $100 \times$; (b) $500 \times$; (KCnt: 1000 counts).

3.2. Thermodynamics Analysis of Reaction Process

As shown in Figure 1, the Mn in cobalt-rich crusts existed in form of manganite (MnO(OH)). However, some previous researchers thought the Mn in cobalt-rich crusts had a valency of 4 and could exist in form of manganese dioxide (MnO₂) [30]. Based on this research, the main reactions of Mn, which had a valency of 4 or 3 reacted with sulfuric acid and carbon in the acid baking process, were expressed as Equation (1) to Equation (6) (Table 2). We performed the thermodynamic calculation for these main reactions of Mn in the acid baking process, and the standard Gibbs free energy changes of main reactions in the acid baking process were calculated by HSC 6.0 software (HSC Chemistry 6.0, 2006, Metso Outotec Finland Oy, Lokomonkatu, Finland) [31].

Table 2. The main reactions in acid baking process.

No.	Reaction Formulas
(1)	$\frac{1}{4}C + H_2SO_4 + MnO \cdot OH = MnSO_4 + \frac{3}{2}H_2O + \frac{1}{4}CO_2(g)$
(2)	$H_2SO_4 + MnO \cdot OH = MnSO_4 + \frac{3}{2}H_2O + \frac{1}{4}O_2(g)$
(3)	$\frac{1}{4}C + MnO \cdot OH = MnO + \frac{1}{2}H_2O + \frac{1}{4}CO_2(g)$
(4)	$\frac{1}{2}C + H_2SO_4 + MnO_2 = MnSO_4 + H_2O + \frac{1}{2}CO_2(g)$
(5)	$H_2SO_4 + MnO_2 = MnSO_4 + H_2O + \frac{1}{2}O_2(g)$
(6)	$\frac{1}{2}C + MnO_2 = MnO + \frac{1}{2}CO_2(g)$
(7)	$FeO \cdot OH + \frac{3}{2}H_2SO_4 = \frac{1}{2}Fe_2(SO_4)_3 + 2H_2O$

The standard Gibbs free energy changes (ΔG^{θ}) are plotted as a function of temperature in Figure 4 for Equations (1) to (6), showing that the standard Gibbs free energies of all reactions are less than 0 kJ/mol in the temperature range from 273 K to 573 K. It means that the all reactions of manganese minerals during the sulfuric acid baking process can occur spontaneously. However, in the absence of sulfuric acid, manganite (MnO(OH)) or manganese oxide (MnO₂) can react difficultly with carbon under these ranges of temperature [32]. It can be found easily in Figure 3 that the standard Gibbs free energies of Equations (1) and (4) are significantly lower than that of Equations (2) and (5). It means that the manganese minerals in cobalt-rich crusts, which maybe exist in form of manganite (MnO(OH)) ore manganese dioxide (MnO₂), can react with sulfuric acid easier when the carbon is added during the sulfuric acid baking process. Therefore, it could be learned from the thermodynamics analysis that carbon could promote the reactions of manganese minerals with sulfuric acid directly or indirectly.



Figure 4. Temperature effects on the standard Gibbs free energy changes for main reactions.

3.3. The Sulfuric Acid Baking Process

3.3.1. Effect of Carbon during Sulfuric Acid Baking Process

It has always been known that the cobalt-rich crust comprises some oxides such as MnO(OH), FeO(OH), NiO, Co₂O₃, CaO, etc. However, the leaching ratio of Fe in FeOOH is approximately 60% at an acid/solid ratio of 1.0 during the acid baking process [27]. Hence, the theoretical ratio of acid/crust is approximate 0.67 when the leaching ratio of Fe is 60%. Finally, in order to determine the effect of carbon at low and high sulfuric acid consumption during the acid baking process, we determine that the excess coefficients of theoretical ratio A/C are 1.1(an A/C of 0.733) and 0.55 (an A/C of 0.367), respectively. Due to the exothermic reactions between oxides and sulfuric acid, the temperature of the mixture can reach $100 \sim 110^{\circ}$ C during the mixing process of crust and sulfuric acid. Considering the exothermic reactions and previous research [33], we finally determine the sulfuric acid temperatures of 110 and 200° C, respectively.

The effects of carbon on the leaching ratio during the acid baking process are presented in Figure 5. We can find that carbon is a key factor in the leaching ratios of Mn. The leaching ratios of Mn increase by approximately 33% and 25% under the mass ratio of acid and crust of 0.733, respectively, when the acid baking temperatures are 110 °C and 200 °C with and without carbon (Figure 5a,c). Meanwhile, the XRD patterns of these leaching residues under the A/C ratio of 0.733 at a temperature of 110 °C and 200 °C are analyzed (Figure 6a,c). The results show that the diffraction peak intensities of pyrolusite (MnO₂) (PDF#72-1983) decrease significantly when the carbon exists during acid baking. The weakened diffraction peaking of pyrolusite indicated the carbon could promote the reactions of Mn minerals in cobalt-rich crust and sulfuric acid during acid baking. It can be noted that the obvious diffraction peak of carphosiderite $[(H_3O)Fe^{3+}_3(SO_4)_2(OH)_6]$ (PDF#18-0653) is founded in leaching residues when the carbon exists during acid baking (Figure 6a,c). The existence of carbon during the acid baking process possibly promotes the transformation from FeO(OH) to carphosiderite in the leaching process.



Figure 5. Effects of carbon during acid baking process. (a) A/C ratio = 0.733, T = 110 °C; (b) A/C ratio = 0.367, T = 110 °C; (c) A/C ratio = 0.733, T = 200 °C; (d) A/C ratio = 0.367, T = 200 °C).



Figure 6. XRD patterns of leaching residues. (a) A/C ratio = 0.733, T = 110 °C; (b) A/C ratio = 0.367, T = 110 °C; (c) A/C ratio = 0.733, T = 200 °C; (d) A/C ratio = 0.367, T = 200 °C; (black line: carbon, red line: no carbon).

Compared with the A/C ratio of 0.733, different results during the acid baking process are found when the A/C ratio is 0.367. The leaching ratios of Co increase by approximately 14% when the acid baking temperatures are 110 °C and 200 °C with and without carbon (Figure 5b,d). The leaching ratio of Mn can only reach 45%, increasing the temperature cannot improve the leaching ratio of Mn. The low leaching ratio of Mn demonstrates that the effect of carbon on the leaching of Mn is limited when the mass ratio of acid and crust declines. The reason for the decrease in the Mn leaching ratio may be ascribed to the fact that there is not enough sulfuric acid to react with carbon and cobalt-rich crust to form MnSO₄ during the acid baking process. The XRD patterns of leaching residues also confirm the results of experiments (Figure 6b,d). The diffraction peak of pyrolusite (MnO₂) can be still found in leaching residues when the carbon exists during the acid baking process, and the diffraction peak of pyrolusite discovered in the leaching residue indicate that the Mn minerals are not decomposed during the acid baking process.

In the acid baking process, a portion of calcium in a cobalt-rich crust reacts with sulfuric acid to form the calcium sulfate/anhydrite (calcium sulfate: PDF#74-1728; anhydrite: PDF#72-0916), and the other part of calcium in the cobalt-rich crust reacts with sulfuric acid and manganese to form the despujolsite $[Ca_3Mn(SO_4)_2OH_6\cdot(H_2O)]$ (PDF#72-0388) which exist in leaching residues. Figure 6b,d indicate that a small amount of manganese in leaching residues exists in form of wad $[MnO_2\cdot MnO\cdot H_2O]$ (PDF#02-1070).

3.3.2. Effect of Carbon at Low Temperature and Low Acid Consumption

The effects of carbon on the leaching ratio of elements at the temperature of 110 $^{\circ}$ C and the A/C ratio of 0.367 are presented in Figure 7; obviously, the promotion of carbon on the leaching ratio of elements in the cobalt-rich crust is limited with these acid baking

conditions. Due to the low A/C ratio, there is not enough H_2SO_4 to react with carbon and MnO_2 or MnO(OH) to form the $MnSO_4$. It has been testified by the thermodynamic analysis in Section 3.2 that the carbon cannot reduce completely the high valence Mn and the high valance Co in the cobalt-rich crust at low temperature, due to insufficient H_2SO_4 during the acid baking process. Therefore, the leaching ratios of Mn and Co do not increase with increasing the mass ratio of carbon and crust. However, it can be seen in Figure 6 that the Ni in the cobalt-rich crust is easier to be leached than the Co and Mn. The higher leaching ratio of Ni indicates that Ni exists in the form of a low valance state in a cobalt-rich crust.



Figure 7. Effects of carbon on leaching ratio of the elements (A/C = 0.367, T = $110 \degree$ C).

3.3.3. Effect of Carbon at Moderate Temperature and Low Acid Consumption

The effects of carbon on the leaching ratio of elements at the temperature of 200 °C and the A/C ratio of 0.367 are presented in Figure 8. Compared with the results at the temperature of 110 °C, the promotion of carbon on the leaching ratio of elements in the cobalt-rich crust is improved when the acid baking conditions are at a temperature of 200 °C and the A/C ratio of 0.367. The leaching ratio of Mn increases with increasing the mass ratio of carbon and crust, and the leaching ratio of Mn has reached 57.16% when the mass ratio of carbon and crust is 0.4. The higher leaching ratio of Mn at 200 °C than that at 110 °C demonstrated that the higher baking temperatures could promote the formation of MnSO₄, generated from reactions between MnO(OH) or MnO₂ with carbon and sulfuric acid during acid baking. However, the leaching ratio of Co does not increase much more after the mass ratio of carbon and crust increases by 0.2. The steady leaching ratio of Co illustrates that the promotion effect of carbon is limited, due to the lower mass ratio of the A/C.



Figure 8. Effects of carbon on leaching ratio of the elements (A/C = 0.367, T = 200 $^{\circ}$ C).

Based on the results of Figures 7 and 8, the leaching ratios of Ni and Co have reached 97.36%, 76.79% at 110 °C, and 94.21%, 78.95% at 200 °C, respectively, when the mass ratio

of carbon and crust is 0.1. Therefore, the mass ratio of carbon and crust of 0.1 is selected for subsequent experiments.

3.3.4. Effect of Mass Ratio of Acid and Crust

Figure 9 shows the effects of acid consumption on the leaching ratio of elements at the temperature of 200 °C and the mass ratio of carbon and crust of 0.1. We found that acid consumption is another key factor in the leaching ratio of Mn, Co, and Fe. The leaching ratios of Mn and Fe increase significantly with increasing the A/C ratio, and the leaching ratios of Mn and Fe reached 61.69% and 80.32% when the A/C ratio reached 0.733. However, there is no significant increase in the leaching ratios of Ni and Co after the A/C ratio reached 0.567. Meanwhile, the leaching ratios of Ni and Co reached 95.16% and 92.17%, respectively, and the leaching ratio of Fe is just 26.83%. To avoid a lot of ferrous minerals to be leached into the leachate, the A/C ratio of 0.567 is selected as the optimal acid consumption parameter.



Figure 9. Effects of acid consumption on leaching ratio of the elements. (Mass ratio of carbon and crust = 0.1, T = $200 \degree$ C).

3.4. Comprehensive-Factor Experiment

Table 3 shows the results of three groups of verification tests under the conditions of a temperature of 200 °C, a time of 240 min, an A/C ratio of 0.567, and a mass ratio of carbon and crust of 0.1. It can be seen that the average leaching ratios of Ni, Co, and Cu can reach 98.59%, 91.62%, and 93.81%, respectively, and the average leaching ratios of Mn and Fe are just 41.27% and 26.94%, respectively. The stable and high leaching ratios of Ni, Co, and Cu prove the stability of the acid baking technique.

Table 3. Comprehensive-factor experimental results. (T = 200 $^{\circ}$ C, t = 240 min, A/C ratio = 0.567, Mass ratio of carbon and crust).

Samples –		Content of	Elements in	Residue/%		Leaching Ratio/%				
	Ni	Со	Cu	Mn	Fe	Ni	Со	Cu	Mn	Fe
1	0.0089	0.055	0.0094	14.84	15.79	98.38	92.40	93.63	45.11	27.20
2	0.0079	0.058	0.0094	15.99	15.85	98.55	91.94	93.59	40.49	26.46
3	0.0062	0.067	0.0083	16.3	15.41	98.84	90.51	94.23	38.20	27.17
average	0.0077	0.06	0.0090	15.71	15.68	98.59	91.62	93.81	41.27	26.94

In order to obtain the pure Ni, Co, Cu, and Mn sulfate solution, Fe in the acid bakingleaching liquor needs to be removed first by precipitation. The Ni, Co, and Cu sulfides can be obtained by the sulfide precipitation after the removal of Fe. Finally, the separation of Ni, Co, and Cu can be accomplished by the sulfuric acid leaching and solvent extraction process [34,35]. The leaching residue could be separated and recovered by the roasting and



magnetic separation technique [36]. The schematic flow sheet of this technique is presented in Figure 10.

Figure 10. The schematic flow sheet of this technique.

4. Discussion

Figure 11 displays the scanning images of the cobalt-rich crust leaching residues during the acid baking process, with and without carbon, under optimal conditions in this technique. We found the leaching residue particles during the acid baking process with carbon are more complete than that without carbon. As shown in Figure 11a–c, a large part of leaching residues after the acid baking process with carbon are completed particles. The completed particles indicate that the cobalt-rich crust particles are not destroyed completely by sulfuric acid when carbon is added in the acid baking process. However, we easily found that a large number of leaching residues after the acid baking process without carbon have become the porous particles in Figure 11d–f, which may explain why the sulfuric acid corrodes the FeO(OH) more easily in the cobalt-rich crust during the acid baking process without carbon. The thermodynamic analysis results in Figure 4 demonstrate that H_2SO_4 reacts with FeO(OH) more easily than that with MnO(OH) when there is no carbon added in the acid baking process (as can be seen in Figure 4, the ΔG of Equation (7) is lower than that of Equation (2)). However, the ΔG of Equation (1) is lower than that of Equation (7), demonstrating that MnO(OH) reacts with H₂SO₄more easily than FeO(OH) when there is carbon in the acid baking process. Combined with the higher content of Fe in the EDS results of Figure 12 (Table 4) than that of Figure 13 (Table 5), we could confirm completely that carbon significantly promotes the reactions between MnO(OH) and sulfuric acid during the acid baking process, with the same amount of sulfuric acid.



Figure 11. The scanning images of leaching residues: (a–c) carbon; (d–f) no carbon.



Figure 12. Cont.



Figure 12. The SEM and EDS of leaching residues during acid process with carbon. (KCnt: 1000 counts).

Table 4. Typical elemental compositions (wt%) of selected points as determined by SEM-EDS analysis (corresponding to Figure 12).

Points	0	Si	Р	S	Ti	Mn	Fe	Cu	Ca	Na	Al	К
1	9.61	2.32	1.99	3.08	3.82	53.99	22.84	2.36				
2		18.30		7.43	4.67	30.60	20.99	5.48	4.00			1.53
3	14.19	2.47	2.27	2.96	4.17	50.40	21.20	2.34				
4	34.00	55.07								3.58	7.36	

Table 5. Typical elemental compositions (wt%) of selected points as determined by SEM-EDS analysis (corresponding to Figure 13).

Points	0	Si	Р	S	Ti	Mn	Fe	Cu
1	15.41	8.49	1.75	2.43	3.33	55.54	11.10	1.95
2	9.50	7.89	2.12	1.88	4.09	58.51	13.06	2.95
3	13.17	9.08	1.07	2.24	1.97	59.20	10.33	2.93
4	39.81	60.19						



Figure 13. The SEM and EDS of leaching residues during acid process without carbon. (KCnt: 1000 counts).

Figures 12 and 13 show the SEM of leaching residues during the acid baking process, with and without carbon, under optimal conditions and the EDS results show the elemental compositions of the points corresponding to the SEM. As can be seen, the main compositions of leaching residues are iron and manganese oxides and silicon dioxide. Combined with the experimental result in Figure 5, the higher content of Fe and lower content of Mn in Figure 12 than in Figure 13 confirms that the carbon obviously promotes the reactions between sulfuric acid and MnO(OH) in the cobalt-rich crust.

Figure 14 presents the gas compositions during the acid baking process, with and without carbon. It was found that the gas component of exhausted gas is CO_2 during acid baking and SO_2 was not detected during acid baking. The concentration of CO_2 increased from 30 ppm to 120 ppm as the time increased from 0 to 10 min at the temperature of 200 °C during the acid baking without carbon (Figure 14b). The concentration of CO_2 decreased further over time. It can be inferred that the CO_2 was generated from the reactions between H_2SO_4 and a small amount of C which exist in the cobalt-rich crust during acid baking without carbon.



Figure 14. The gas analysis at optimal parameter during acid baking process: (a) carbon; (b) no carbon.

As can be seen in Figure 14, the concentration of CO_2 increased significantly when the anthracite was added to the acid baking process and the concentration of CO_2 reached 400 ppm (Figure 14a). Meanwhile, the CO was still detected in spite of lower content. A large amount of CO_2 and a small amount of CO in the exhausted gas illustrates that the carbon directly participated in the reactions between H₂SO₄ and MnO(OH). Furthermore, the undetected SO₂ in exhausted gas confirms well that the carbon participated in the reactions directly rather than indirectly. These things considered, the reactions between H₂SO₄ and C as well MnO(OH) during the acid baking process maybe comprised of the Reactions (8) and (9) (Table 6).

Table 6. The main reactions between carbon and MnO(OH) as well as H_2SO_4 in acid baking process.

No. Reaction Formulas					
(8)	$C + 2MnO(OH) + 2H_2SO_4 = 2MnSO_4 + 3H_2O + CO(g)$				
(9)	$C + 4MnO(OH) + 4H_2SO_4 = 4MnSO_4 + 6H_2O + CO_2(g)$				

5. Conclusions

The valuable metal recovery process from a cobalt-rich crust by carbon as a reduction agent was a facile and environment-friendly alternative technology. The thermodynamic results demonstrated that carbon could promote the reactions of manganese minerals with sulfuric acid directly or indirectly. The diffraction peak of pyrolusite disappeared in the leaching residue indicating that the Mn minerals were decomposed during the acid baking process at an A/C ratio of 0.733 when the carbon existed during the acid baking process. The experimental results indicate that the average leaching ratios of Ni, Co, and Cu can reach 98.59%, 91.62%, and 93.81%, respectively, and the average leaching ratios of Mn and Fe are just 41.27% and 26.94%, respectively, under the conditions of a temperature of 200 °C, a time of 240 min, an A/C ratio of 0.567, and mass ratio of carbon and crust of 0.1.

Author Contributions: Conceptualization, X.J.; methodology, X.J. and D.L; validation, D.L and S.W.; formal analysis, X.S. and F.Z.; investigation, L.F.; writing—original draft preparation, D.L.; writing—review and editing, L.F. and D.Z. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by China Ocean Mineral Resources Research and Development Association, grant number JS-KTHT-2019-01.

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

References

- Fu, X.; Beatty, D.N.; Gaustad, G.G.; Ceder, G.; Roth, R.; Kirchain, R.E.; Bustamante, M.; Babbitt, C.; Olivetti, E.A. Perspectives on Cobalt Supply through 2030 in the Face of Changing Demand. *Environ. Sci. Technol.* 2020, 54, 2985–2993. [CrossRef] [PubMed]
- 2. Alves Dias, P.; Blagoeva, D.; Pavel, C.; Arvanitidis, N. Cobalt: Demand-supply balances in the transition to electric mobility. *Publ. Off. Eur. Union* **2018**, *10*, 97710.
- 3. Geological Survey. Mineral Commodity Summaries 2021; U.S. Geological Survey: Reston, VA, USA, 2021; pp. 154–196.
- 4. Hariprasad, D.; Mohapatra, M.; Anand, S. Reductive Leaching of Manganese Nodule Using Saw Dust in Sulphuric Acid Medium. *Trans Indian Inst. Met.* **2018**, *71*, 2971–2983. [CrossRef]
- 5. Cronan, D.S. Underwater Minerals; Academic Press: London, UK, 1980; p. 362.
- 6. Cronan, D.S. Criteria for the recognition of areas of potentially economic manganese nodules and encrustations in the CCOP/SPOAC region of the central and southwestern tropical pacific. *South Pac. Mar. Geol. Notes* **1984**, *3*, 1–17.
- Pichocki, C.; Hoffert, M. Characteristics of Co-rich ferromanganese nodules and crusts sampled in French Polynesia. *Mar. Geol.* 1987, 77, 109–119. [CrossRef]
- Halbach, P. Co-Rich Ferromanganese Seamount Deposits of the Central Pacific Basin, Halbach Peter and Winter Peter's Marine Mineral Deposits-New Research Results and Economic Prospects, Marine Rohstoffe und Meersetechnik, Bd 6; Verlag Gluckkauf: Essen, Germany, 1982; pp. 60–85.
- 9. Clark, A.; Johnson, C.; Chinn, P. Assessment of Cobalt-Rich Manganese Crusts in the Hawaiian, Johnston and Palmyra Island's Exclusive Economic Zones; Natural Resources Forum: New York, NY, USA, 1984; Volume 8, pp. 163–174.
- 10. Manheim, F.T. Marine Cobalt Resources. Science 1986, 232, 600–608. [CrossRef] [PubMed]
- 11. 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]
- 12. Ito, M.; Tsunekawa, M.; Yamaguchi, E.; Sekimura, K.; Kashiwaya, K.; Hori, K.; Hiroyoshi, N. Estimation of degree of liberation in a coarse crushed product of cobalt-rich ferromanganese crust/nodules and its gravity separation. *Int. J. Miner. Processing* **2008**, *87*, 100–105. [CrossRef]
- Premchand; Jana, R.K. Processing of polymetallic sea nudules: An overview. In Proceedings of the third (1999) Ocean Mining Symposium, Goa, India, 8–10 November 1999; pp. 237–245.
- 14. Zubkov, M.V.; Plucinski, P.K.; Dartiguelongue, A.C.Y.; Lusty, P.A.J. Metal Extraction from Deep-Ocean Mineral Deposits. *Elements* **2018**, *14*, 319–324. [CrossRef]
- 15. Zhao, F.; Jiang, X.; Wang, S.; Feng, L.; Li, D. The Recovery of Valuable Metals from Ocean Polymetallic Nodules Using Solid-Stade Metalized Reduction Technology. *Minerals* **2020**, *10*, 2–15.
- Stefanova, V.P.; Iliev, P.K.; Stefanov, B.S.; Avram, G. Selective Dissolution of FeCuNiCoMn alloy Obtained after Pyrometallurgical Processing of Polymetallic Nodules. In Proceedings of the eighth (2009) Ocean Mining Symposium, Chennai, India, 20–24 September 2009; pp. 186–190.
- 17. Su, K.; Ma, X.; Parianos, J.; Zhao, B. Thermodynamic and Experimental Study on Efficient Extraction of Valuable Meals from Polymetallic Nodules. *Minerals* **2020**, *10*, 360. [CrossRef]
- Wang, Y.; Li, Z.; Li, H. A new process for leaching metal values from ocean polymetallic nodules. *Miner. Eng.* 2005, 18, 1093–1098. [CrossRef]
- 19. Mittal, N.K.; Sen, P.K. India's first medium scale demonstration plant for treating poly-metallic nodules. *Miner. Eng.* 2003, 16, 865–868. [CrossRef]
- Anand, S.; Das, S.C.; Das, R.P.; Jena, P.K. Leaching of Manganese Nodules at Elevated Temperature and Pressure in the Presence of Oxygen. *Hydrometallurgy* 1988, 20, 155–168. [CrossRef]

- 21. Mehta, K.D.; Das, C.; Kumar, R.; Pandey, B.D.; Mehrotra, S.P. Effect of mechano-chemical activation on bioleaching of Indian Ocean nodules by a fungus. *Miner. Eng.* **2010**, *23*, 1207–1212. [CrossRef]
- 22. Dennis, M.; Charlotte, K.; Andrea, K. 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.
- Randhawa, N.S.; Hait, J.; Jana, R.K. A brief overview on manganese nodules processing signifying the detail in the Indian context highlighting the international scenario. *Hydrometallurgy* 2015, 165, 166–181. [CrossRef]
- Jana, R.K.; Pandey, B.D.; Premchand. Ammoniacal leaching of roasting reduced deep-sea manganese nodules. *Hydrometallurgy* 1999, 53, 45–56. [CrossRef]
- Acharya, R.; Ghosh, M.K.; Anand, S.; Das, R.P. Leaching of metals from Indian ocean nodules in SO₂-H₂O-H₂SO₄-(NH₄)₂SO₄medium. *Hydrometallurgy* 1999, 53, 169–175. [CrossRef]
- Niinae, M.; Komatsu, N.; Nakahiro, Y.; Wakamatsu, T.; Shibata, J. Preferential leaching of cobalt, nickel and copper from cobalt-rich ferromanganese crusts with ammoniacal solutions using ammonium thiosulfate and ammonium sulfite as reducing agents. *Hydrometallurgy* 1996, 40, 111–121. [CrossRef]
- Inoue, A.; Kawahara, M. Ammoniacal leaching and solvent extraction of cobalt crusts using sulfur dioxide gas. *Shigen Sozai* 1998, 114, 195–199. [CrossRef]
- Allen, H.P.; Abercrombie, H.L.; Rice, D.A. Leaching and recovery of metals from cobalt-rich manganese ocean crust. *Miner. Metall. Processing* 1991, *8*, 97–104. [CrossRef]
- 29. Hein, J. Cobalt-rich ferromanganese crusts: Global distribution, composition, origin and research activities. In *Minerals Other than Polymetallic Nodules of the International Seabed Area;* International Seabed Authority: Kingston, Jamaica, 2004.
- 30. Ju, J.R.; Feng, Y.L.; Li, H.R.; Yu, H.; Wu, H.; Liu, S.L. The limiting effect of manganese phase of oceanic cobalt-rich crust reduction by sawdust in acid leaching. *Sustain. Chem. Pharm.* **2021**, *19*, 100346. [CrossRef]
- 31. HSC Chemistry 6.0. *Chemical Reaction and Equilibrium Software with Extensive Termochemical Database and Flowsheet Simulation, Ver.* 6.0; Outokumpu Research Oy: Pori, Finland, 2006.
- 32. Seşen, F.E. Practical reduction of manganese oxide. J. Chem. Technol. Appl. 2017, 1, 1–2.
- Kim, R. Effect of Sulfuric Acid Baking and Caustic Digestion on Enhancing the Recovery of Rare Earth Elements from a Refractory Ore. *Minerals* 2020, 10, 532. [CrossRef]
- 34. Ochromowicz, K. Recent Advancements in Metallurgical Processing of Marine Minerals. Minerals 2021, 11, 1437. [CrossRef]
- Keber, S.; Brückner, L.; Elwert, T.; Kuhn, T. Concept for a Hydrometallurgical Processing of a Copper-Cobalt-Nickel Alloy Made from Manganese Nodules. *Chem. Tech.* 2020, 92, 379–386. [CrossRef]
- 36. Yuan, S. An innovative technology for full component recovery of iron and manganese from low grade iron-bearing manganese ore. *Powder Technol.* **2020**, *373*, 73–81. [CrossRef]