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Waste-to-Resources: Leaching of Cobalt from Spent Cobalt Oxide Catalyst

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Abstract: This article presents studies on the recovery of cobalt from a spent cobalt oxide catalyst, left after the preparation of industrial catalysts. Apart from cobalt, the tested material contained iron, copper, zinc, and nickel. Leaching was proposed as a simple and feasible operation to treat the spent cobalt oxide. The 0.1–8.0 M H_2SO_4 solutions were applied as leaching agents at an ambient temperature and at 70 °C. An 8.0 M H_2SO_4 solution at 70 °C leached two-fold more Co(II) than a 0.1 M H_2SO_4 solution at the same temperature. Similar to Co(II), regardless of the leaching temperature, the Fe ion was leached more efficiently with 4.0 or 8.0 M H_2SO_4 than with a 0.1 M acid. It should be emphasized that the Co(II) content in the solution after leaching was predominant at >90% (~4800 mg/dm^3), compared to other metal ions. The ANOVA analysis indicated that both the sulfuric(VI) acid concentration and temperature had a significant effect on the leaching efficiency. An increase in acid concentration from 0.1 to 8 M and the temperature of leaching (from ambient to 70 °C) had a positive effect on the Co leaching efficiency (an increase from ~20 to almost 50%). The proposed hydrometallurgical treatment of the spent cobalt oxide catalyst is a response to the waste-to-resource (WTR) approach.

Keywords: waste-to-resource (WTR); cobalt recovery; leaching; hydrometallurgy; spent industrial catalyst; cobalt oxide

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1. Introduction

Today, cobalt is considered one of the world's essential elements. For example, in the European Union it is classified as a critical raw material of high economic importance and with a high supply risk [1,2]. Cobalt demand still increases and is expected to quadruple over the next four decades, especially due to the increasing production of lithium-ion batteries (LiBs) [1,3,4], which are crucial for the expansion of electric mobility and digitalization. The cathodes of electric vehicle (EV) batteries are estimated to contain up to 15 kg of cobalt, 40 kg of nickel, and 30–50 kg of lithium [5]. In addition, the high demand for cobalt also results from a growing market for electronics, which is present in every aspect of our lives and more people can now afford such devices. Apart from its application in the production of LiBs, cobalt is very important in metallurgical applications as a component of superalloys, e.g., for turbine engines for aircrafts [6,7], in the chemical industry as catalysts, adhesives, pigments, and sensors [8,9], in the ceramic and enamel industry [9,10], or in medicine [11,12].

Moreover, the risk to cobalt supply is high, since cobalt mining is concentrated in one country, the Democratic Republic of Congo, which is considered a politically unstable region, and cobalt refining is concentrated in the People's Republic of China [3,13]. Therefore, the waste-to-resource (WTR) approach is considered to minimize the supply risk by recycling cobalt from various secondary resources, such as metallurgical waste and spent cobalt compounds, spent LiBs, and spent industrial catalysts [13–17].

Numerous processes have been proposed to recover metals, including cobalt, from spent hydrodesulfurization (HDS) catalysts [18–22]. Such catalysts can be an important secondary resource for Ni, Mo, Co, and Al. HDS catalysts mostly contain Mo with some admixture of Co/Ni deposited on alumina. An exemplary composition of HDS is approximately 8 wt% Mo, 2.5 wt% Co, and 0.05 wt% Ni [23]. Despite the abundance of metals in these spent materials, there are some difficulties in the selective and efficient recovery of each of the metals. These include the accumulation of carbon/organic coke on the catalyst surface, the stability of the metal oxides, or similar chemical properties of the recovered metals.

In most cases, hydrometallurgical operations, such as leaching, precipitation, liquid–liquid extraction, and electrowinning, have been proposed to treat secondary materials containing cobalt [15,18,24,25]. To overcome the difficulties in metal recovery and convert metal oxides to soluble forms, prior to the main process, some pretreatment steps have been implemented, including roasting or calcination [22,26,27]. For example, the use of sodium persulfate ($Na_2S_2O_8$) in the leaching solution to recover Mo, Co, and Ni from spent HDS catalysts roasted at 500 °C resulted in the recovery of 90% Mo, 86.5% Co, and about 80% Ni [22]. Furthermore, the dissolution of a preoxidized catalyst in 9 M H_2SO_4 at 90 °C and subsequent extraction and precipitation allowed Mo, Co, or Ni and Al to be separated with high yields (>98%) [27].

Another approach has been reported by Chauhan et al. [26], who developed a chelant (EDTA)-assisted recovery process to obtain Co and Mo from the spent hydroprocessing catalyst pretreated by calcination at 550 °C. Chelation with EDTA resulted in the separation of Co and Mo from Al and other impurities and led to a recovery of Co and Mo of 80 and 85%, respectively. The recovered Co and Mo were reused by impregnation on the recovered alumina to synthesize a fresh catalyst.

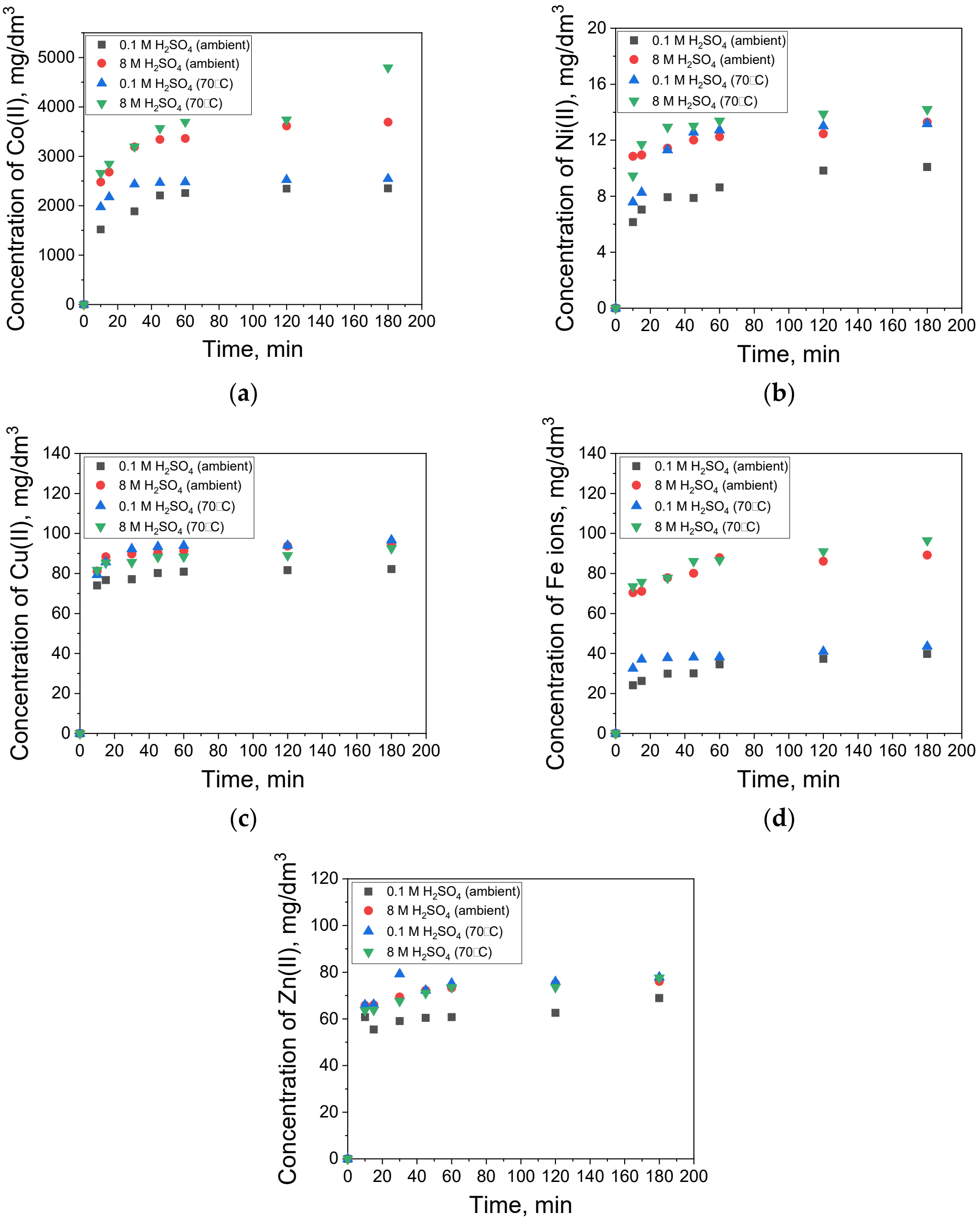
However, in general, spent HDS catalysts were contacted, without pretreatment, with leaching agents mainly with mineral acids (HCl, HNO_3, H_2SO_4, aqua regia) to dissolve metals [18,23,24]. This resulted in lower metal recoveries (near 50%) than from pretreated materials. The highest values of the leaching recovery with 2 M HCl at 60 °C from a spent catalyst from the Pertamina Refinery Unit IV, Cilacap, Indonesia, were 34.66% for Co and 5.03% for Mo [21]. To increase the recovery of valuable metals, different oxidants were added to the leaching solutions. Nonetheless, the presence of an oxidant did not always significantly improve the leaching efficiency of Co and Mo. For example, the leaching recovery with 0.5–5 M H_2SO_4 with or without H_2O_2 did not exceed 20 and 40–45% for Co and Mo, respectively [18].

Various processes for metal recovery from hydrodesulfurization catalysts have been reported, but to the best of our knowledge, there is scarce information on Co recovery from the spent cobalt oxide catalyst left after the preparation of industrial catalysts. Such a spent material is considered as waste that should be disposed of or utilized in another way. Thus, our present study focused on the waste-to-resource approach to recover valuable cobalt from this waste. Therefore, leaching was proposed as a simple and feasible operation to treat the spent cobalt oxide. The research objectives covered investigating the conditions for efficient Co leaching from the spent material without additional oxidants, and an analysis of the effects of the leaching conditions by an ANOVA analysis.

2. Results and Discussion

2.1. Effect of Contact Time and Temperature on Leaching of Co(II), Ni(II), Cu(II), Fe Ions, and Zn(II)

A spent cobalt oxide catalyst provided by a Polish waste treating company contained various admixture metals, such as Al, Fe, Cu, Zn, and Ni (more details about the composition in Section 3), therefore the presence of the ions of these metals was determined in the leachates. The influence of the reaction time on the leaching of Co(II), Ni(II), Cu(II), Fe ions, and Zn(II) from the spent cobalt oxide catalyst at an ambient temperature and at 70 °C is presented in Figure 1.



(**a**) (**b**)

(**c**) (**d**)

(**e**)

Figure 1. Influence of reaction time on leaching of (**a**) Co(II), (**b**) Ni(II), (**c**) Cu(II), (**d**) Fe ions, and (**e**) Zn(II) from spent cobalt oxide catalyst at an ambient temperature and at 70 °C (concentrations of H_2SO_4 were 0.1 and 8.0 M).

Regardless of the leaching temperature and the metal leached, the concentration of metal ions increased significantly in the leach solution during the first 10 min of the reaction. After 60 min of leaching, the concentrations changed slightly and reached a plateau. Therefore, the leaching experiments were conducted for no more than 180 min. Furthermore, it was found that the H_2SO_4 concentration rather than the leaching temperature had a considerable influence on the leaching of cobalt and iron from the catalyst. The concentration of Co(II) after leaching with 8.0 M H_2SO_4 was approximately 4800 mg/dm^3, while after leaching with 0.1 M acid it reached approximately 2500 mg/dm^3 Co(II) (Figure 1a). The concentration of Fe ions was equal to 40 and 80 mg/dm^3 for leaching with 0.1 and 8.0 M H_2SO_4, respectively (Figure 1d). The leaching temperature and the concentration of H_2SO_4

appear to have a slight influence on the leaching of Cu(II) (Figure 1c) and much less on the leaching of Zn(II) (Figure 1e). Compared to the amount of other metal ions, the Ni(II) concentration was the lowest, and reached less than 20 mg/dm^3 (Figure 1b), but it should be emphasized that the Ni content in the catalyst was lower than that of the other metals analyzed.

The content of metal ions in the solution after 180 min of leaching with 8.0 M H_2SO_4 at both temperatures is presented in Table 1.

Table 1. Composition of the solution after 180 min of leaching with 8.0 M H_2SO_4.

Temperature, °C	**Content, %**					
	Co(II)	**Ni(II)**	**Cu(II)**	**Fe Ions**	**Zn(II)**	**Al(III)**
22	90.5	0.3	2.3	2.2	1.9	2.8
70	92.3	0.3	1.8	1.9	1.5	2.3

The preliminary results showed a predominant content of Co(II) (>90%) in the solution after leaching compared to other metal ions, which was expected due to the predominance of cobalt in this catalyst (for the composition of the catalyst, see Section 3.1).

2.2. *Effect of H_2SO_4 Concentration and Temperature on Leaching of Co(II), Ni(II), Cu(II), Fe Ions, Zn(II), and Al(III)*

As the preliminary leaching of metals with 0.1 and 8 M H_2SO_4 showed that a high acid concentration was more efficient, an investigation with various acid solutions was carried out to find the best concentration of the leaching agent. The concentrations of Co(II) in the solutions after leaching with 0.1–8.0 M H_2SO_4 at both temperatures are presented in Figure 2.

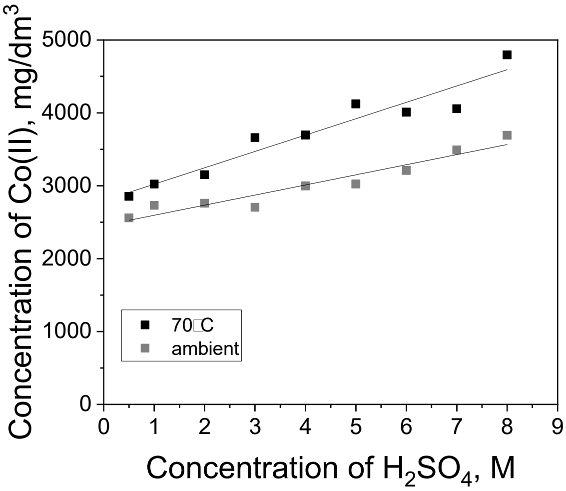
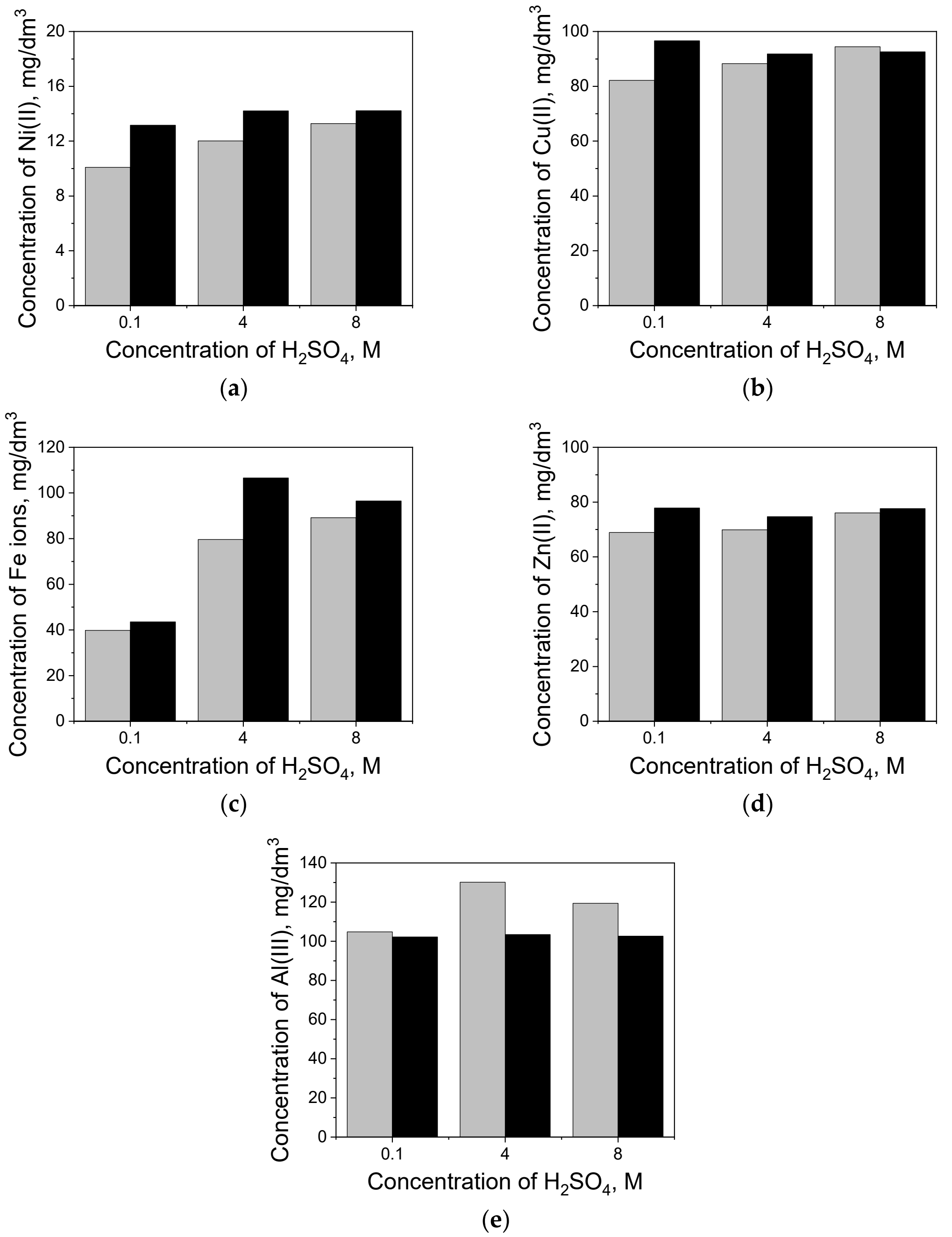


Figure 2. Effect of H_2SO_4 concentration and temperature on the leaching of Co(II) after 180 min at (▨) an ambient temperature and at (■) 70 °C. Concentrations of H_2SO_4 were in the range from 0.1 to 8.0 M, S/L = 1/50 g/cm^3.

The concentration of Co(II) increased linearly with the increasing concentration of H_2SO_4 in the leaching solution. To improve the efficiency of Co(II) leaching (especially at a high concentration of H_2SO_4, 5.0–8.0 M), the reaction must be carried out at an elevated temperature (70 °C). The reaction occurring during the leaching of cobalt(II) oxide with sulfuric(VI) acid is as follows:

$$CoO + H_2SO_4 \rightarrow CoSO_4 + H_2O \quad (1)$$

The concentrations of Ni(II), Cu(II), Fe ions, Zn(II), and Al(III) after 180 min of leaching with 0.1, 4.0, and 8.0 M H_2SO_4 at both temperatures are presented in Figure 3. The leaching results with other H_2SO_4 solutions are presented in Table A1 in the Appendix A.



(**a**) (**b**) (**c**) (**d**) (**e**)

Figure 3. Effect of the H_2SO_4 concentration and temperature on leaching of (**a**) Ni(II), (**b**) Cu(II), (**c**) Fe ions, (**d**) Zn(II), and (**e**) Al(III) after 180 min at (▨) an ambient temperature and at (■) 70 °C. The concentrations of H_2SO_4 were 0.1, 4.0, and 8.0 M, S/L = 1/50 g/cm^3.

Generally, the temperature and concentration of H_2SO_4 appeared to have a slight influence on the leaching of Cu(II), Zn(II), and Al(III) (Figure 3b–e). A significant acid concentration effect was observed for Fe ions. Regardless of the leaching temperature, Fe ion leaching was twice as high with 4.0 or 8.0 M H_2SO_4 than with 0.1 M acid.

To the best of our knowledge, on the one hand, most research on Co recovery by leaching is carried out on spent hydrotreating catalysts, i.e., Mo–Co or Mo–Co–Ni. For example, solutions of 0.5–5.0 M sulfuric(VI) acid (with or without the addition of H_2O_2)

were used for the leaching of metal ions from a spent industrial Co–Mo hydrotreating catalyst in our previous research [18]. The percentage composition of the solution after leaching with 1.0 M H_2SO_4 at 55 °C (S/L = 1/20 g/cm^3) was 43.6, 35.3, and 4.5% for Al(III), Mo(VI), and Co(II), respectively. Moreover leaching with 0.5 M H_2SO_4 resulted in almost 10 g/dm^3 Al(III), 6 g/dm^3 Mo(VI), and 1 g/dm^3 Co(II) in leachate. The low leaching efficiency of Co(II) may have been due to the low content of cobalt (12.4%) and the high content of aluminum (46.6%) and molybdenum (35.9%) in the spent Co–Mo catalyst. As a consequence of such a composition of the Co–Mo catalyst, the leaching of Al(III) and Mo(VI) was favorable. On the other hand, $LiCoO_2$ from LiBs seems to be a valuable perspective resource of cobalt [15]. Despite the fact that Umicore and Inmetco companies operate LiB recycling installations [28], in general, the LiB recycling and metal recovery technologies appear to be still in an early stage of development. Therefore, numerous and varied proposals have ranged from pyrometallurgy [29], hydrometallurgy [28,30], and a combination of both [31,32] to electrometallurgy [33]. Among them, a novel system using deep eutectic solvent (N-methylurea–acetamide) as a leaching solution has been reported to recover 97% of the cobalt from lithium cobalt-oxide-based LiBs and reuse this metal in new batteries [30]. Furthermore, a system of 0.5 M HCl and 0.5 M L-ascorbic acid has been shown to perform ultra-fast leaching of spent cathode materials (97.72% Li and 97.25% Co leached in the S/L ratio: 10 g/L, at 90 °C in 10 min) [28].

2.3. Leaching Efficiency of Co(II), Ni(II), Cu(II), Fe Ions, Zn(II), and Al(III)

A total of 0.5 g of powdered catalyst was mineralized in 5 cm^3 of aqua regia (ambient temperature, 24 h) to determine the metal content in the spent catalyst. The content of metal ions in the solution after mineralization is presented in Table 2. Note that the amount of Co(II) in the solution after mineralization was much higher than the amount of ions of other metals.

Table 2. Mass of Co(II), Ni(II), Cu(II), Fe ions, Zn(II), and Al(III) in the solution after mineralization (calculated per 1 g of the mineralized catalyst).

Mass of Metal Ions after Mineralization, mg					
Co(II)	**Ni(II)**	**Cu(II)**	**Fe ions**	**Zn(II)**	**Al(III)**
492.4	2.0	12.3	18.1	14.4	26.2

The values of the leaching efficiency (Le) of Co(II), Ni(II), Cu(II), Fe ions, Zn(II), and Al(III) after 180 min of leaching with 0.1, 4.0, and 8.0 M H_2SO_4 at both temperatures are presented in Table 3. The L values for leaching with other H_2SO_4 solutions are presented in Table A2 in the Appendix A.

Table 3. Average values of leaching efficiency of Co(II), Ni(II), Cu(II), Fe ions, Zn(II), and Al(III) after 180 min of leaching (ambient temperature and 70 °C, S/L = 1/50 g/cm^3, concentration of H_2SO_4 was 0.1, 4.0, and 8.0 M).

Concentration of H_2SO_4, M	**Le, %**					
	Co(II)	**Ni(II)**	**Cu(II)**	**Fe Ions**	**Zn(II)**	**Al(III)**
	Ambient Temperature					
0.1	21.2 ± 0.5	22.9 ± 0.2	28.9 ± 0.8	9.3 ± 0.4	20.6 ± 0.4	18.8 ± 1.2
4.0	26.8 ± 0.3	27.0 ± 0.2	31.6 ± 0.5	19.3 ± 0.3	21.3 ± 0.4	21.9 ± 1.4
8.0	33.2 ± 0.2	20.1 ± 0.2	34.0 ± 0.3	21.6 ± 0.2	23.5 ± 0.4	29.1 ± 1.9
	70 °C					
0.1	23.1 ± 0.3	29.0 ± 0.6	33.9 ± 0.7	10.8 ± 0.2	23.9 ± 0.2	20.8 ± 3.1
4.0	33.0 ± 0.4	32.0 ± 0.7	32.8 ± 0.9	25.9 ± 0.2	22.7 ± 0.2	17.4 ± 2.5
8.0	42.0 ± 0.8	32.9 ± 0.9	32.2 ± 1.2	23.2 ± 0.3	23.5 ± 0.3	19.4 ± 2.2

Using 8.0 M H_2SO_4 at 70 °C, almost 50% of the Co(II) could be leached, which means ~4800 mg/dm^3 Co(II) in the leachate. Regardless of the H_2SO_4 concentration and temperature, 30–35% of Cu(II), 23–33% of Ni(II) and 20–30% of Al(III) were leached. The leaching efficiency of Fe ions with 0.1 M H_2SO_4 at an ambient temperature was poor (<10%). The Co-containing leachate can be applied to the recovery of metallic cobalt by electrowinning. However, impurities (ions of other metals) should be removed prior to electrolysis. In our previous studies, liquid–liquid extraction with Cyanex 272 extractant was shown to be an efficient and selective Co(II) separation method followed by the production of metallic cobalt [34].

Various researchers have reported that an increase in acid concentration (e.g., H_2SO_4, HCl) did not significantly improve the leaching of metals from spent hydrotreating catalysts [19,21]. Therefore, various oxidants (e.g., H_2O_2) or oxidative roasting have been proposed to improve the performance of Co leaching systems [19,35]. However, in our study no additional oxidants were used to simplify the leaching system, which brings environmental and economic advantages.

2.4. Analysis of Interactions (ANOVA Analysis)

The observations presented in the previous sections were statistically analyzed in order to propose a model equation with optimization of the leaching efficiency of metals leached (Co(II)/Ni(II)/Cu(II)/Fe ions/Zn(II)/Al(III)). Equation (2) was used to investigate the main effects of factors A and B (i.e., concentration of sulfuric acid and temperature, respectively), which can influence the yield of leaching, and their interactions AB. Square effects were not taken into account because the application of the factorial design on two levels allows the analysis of only linear relationships.

$$\mathrm{Le} = \mathrm{b_0} + \mathrm{b_A A} + \mathrm{b_B B} + \mathrm{b_{AB} AB} \tag{2}$$

where b_0, b_A, b_B, and b_{AB} are regression coefficients [36].

To determine which effect contributes significantly to the leaching efficiency (Table 4), a variation analysis (ANOVA) was performed using Statistica 13.3 software [37]. The results of the ANOVA for cobalt, nickel, copper, iron, and zinc are presented in Tables 5–7. In the case of aluminum, the analysis of variance did not show any significance of the factors analyzed.

Table 4. Response values obtained from 2^2 designs for each metal (A, B correspond to concentration of H_2SO_4 and temperature, respectively).

No.	**Factors**		**Response Value Le, %**					
	A, M	**B, °C**	**Co(II)**	**Ni(II)**	**Cu(II)**	**Fe Ions**	**Zn(II)**	**Al(III)**
1	8.0	70	42.9 42.1 41.2	32.0 33.0 33.8	33.1 30.8 32.6	23.4 23.3 22.8	23.7 23.3 23.5	17.3 19.2 21.6
2	0.1	70	22.7 23.4 23.1	29.6 28.5 28.9	34.6 33.1 34.0	10.6 11.0 10.8	23.8 24.1 23.7	17.2 22.2 22.9
3	8.0	22	33.0 33.4 33.2	29.9 30.2 30.3	33.8 34.0 34.3	21.6 21.4 21.7	23.2 23.5 23.9	20.1 20.4 16.9
4	0.1	22	21.0 20.8 21.7	22.7 23.2 22.9	29.4 28.0 29.3	9.7 9.4 9.0	21.0 20.5 20.3	17.6 18.7 20.0

Table 5. Results of ANOVA for Co leaching (A: concentration of H_2SO_4; B: temperature) for full factorial 2^2 design.

Effect	Sum of Squares	DF *	Mean Squares	F-Values	*p*-Values
	Co(II)				
A	719.64	1	719.64	2760.22	**$p < 0.0001$**
B	86.33	1	86.33	331.11	**$p < 0.0001$**
AB	36.33	1	36.33	139.36	**$p < 0.0001$**
Pure error	2.09	8	0.26		
Total	844.39	11			
R^2	0.9966				

* Degree of freedom, Note: $p < 0.0001$ is the most significant; $p < 0.01$ is more significant; $p < 0.05$ is significant.

Table 6. Results of ANOVA for Ni and Cu leaching (A: concentration of H_2SO_4; B: temperature) for full factorial 2^2 design.

Effect	Sum of Squares		DF *		Mean Squares		F-Values		*p*-Values	
	Ni(II)	Cu(II)	Ni(II)	Cu(II)	Ni(II)	Cu(II)	Ni(II)	Cu(II)	Ni(II)	Cu(II)
A	92.24	8.86	1	1	92.24	8.86	299.36	13.61	**$p < 0.0001$**	**0.006**
B	59.41	7.20	1	1	59.41	7.20	192.83	11.06	**$p < 0.0001$**	**0.011**
AB	8.13	35.31	1	1	8.13	35.31	26.38	54.25	**$p < 0.0001$**	**$p < 0.0001$**
Pure error	2.47	5.21	8	8	0.31	0.65				
Total	162.25	56.58	11	11						
R^2	0.9791	0.8734								

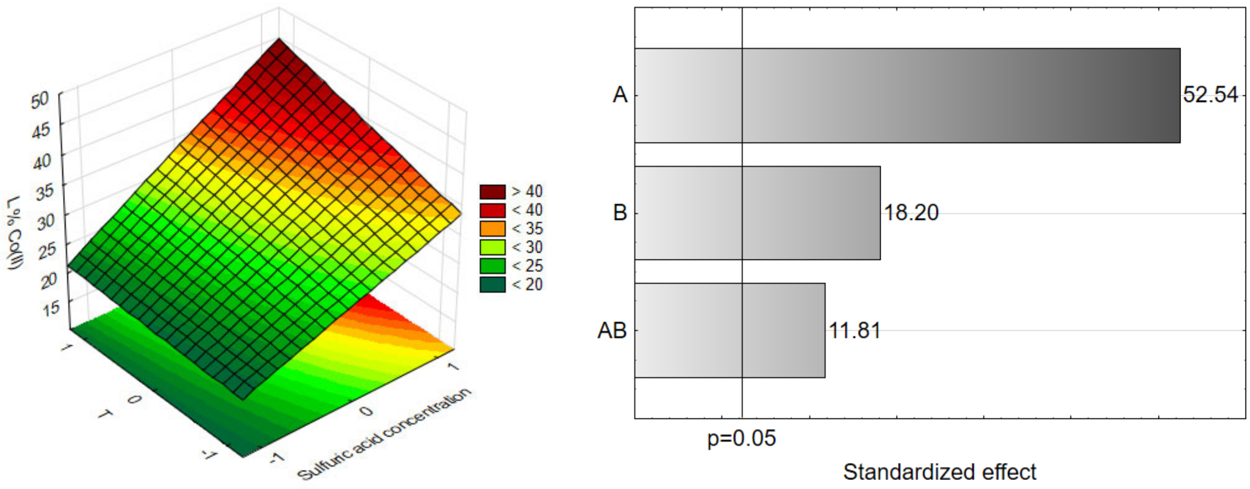
* Degree of freedom, Note: $p < 0.0001$ is the most significant; $p < 0.01$ is more significant; $p < 0.05$ is significant.

Table 7. Results of ANOVA for Fe and Zn leaching (A: concentration of H_2SO_4; B: temperature) for full factorial 2^2 design.

Effect	Sum of Squares		DF *		Mean Squares		F-Values		*p*-Values	
	Fe Ions	Zn(II)	Fe Ions	Zn(II)	Fe Ions	Zn(II)	Fe Ions	Zn(II)	Fe Ions	Zn(II)
A	455.04	4.91	1	1	455.04	4.91	5409.06	51.98	**$p < 0.0001$**	**$p < 0.0001$**
B	6.96	7.73	1	1	6.96	7.73	82.75	81.79	**$p < 0.0001$**	**$p < 0.0001$**
AB	0.01	8.09	1	1	0.01	8.09	0.16	85.57	0.702	**$p < 0.0001$**
Pure error	0.67	0.76	8	8	0.08	0.10				
Total	462.68	21.50	11	11						
R^2	0.998	0.9516								

* Degree of freedom, Note: $p < 0.0001$ is the most significant; $p < 0.01$ is more significant; $p < 0.05$ is significant.

The *p*-value (Tables 5–7) and Pareto diagrams presented in Figure 4 indicate that both the temperature and the sulfuric(VI) acid concentration significantly affect the leaching efficiency of Co(II), Ni(II), Cu(II), Fe ions, and Zn(II), and positively influence the leaching effect of these metals in each case.



(**a**) (**b**)

Figure 4. Response surface plot of the influence of the significant factors (**a**) and the Pareto diagrams (**b**) for all the effects influencing the Le of Co(II).

After the ANOVA analysis, considering the main significant effect and the significant interactions of the main effects in sulfuric(VI) acid leaching solutions, the model equations describing the leaching efficiency of Co(II), Ni(II), Cu(II), Fe ions, and Zn(II) are expressed as follows:

$$\mathrm{Le}_{\mathrm{Co(II)}} = 29.88 + 7.74\mathrm{A} + 2.68\mathrm{B} + 1.74\mathrm{AB} \tag{3}$$

$$\mathrm{Le}_{\mathrm{Ni(II)}} = 28.74 + 2.77\mathrm{A} + 2.23\mathrm{B} - 0.82\mathrm{AB} \tag{4}$$

$$\mathrm{Le}_{\mathrm{Cu(II)}} = 32.25 + 0.86\mathrm{A} + 0.77\mathrm{B} - 1.72\mathrm{AB} \tag{5}$$

$$\mathrm{Le}_{\mathrm{Fe\ ions}} = 16.23 + 6.16\mathrm{A} + 0.76\mathrm{B} \tag{6}$$

$$\mathrm{Le}_{\mathrm{Zn(II)}} = 22.88 + 0.64\mathrm{A} + 0.80\mathrm{B} - 0.82\mathrm{AB} \tag{7}$$

The analysis of the coefficients in the obtained models shows that only in the case of Fe ions did the interaction of variables A and B not have a significant impact on the leaching efficiency. It should be noted that in the case of Ni(II), Cu(II), and Zn(II), despite the positive impact of both analyzed factors, the interaction of these factors had a significant impact, although a negative one, on the leaching efficiency.

3. Materials and Methods

3.1. Reagents and Solutions

The spent cobalt oxide catalyst was provided by a Polish waste treatment company. The percentage content of elements determined by XRF analysis was as follows: 55.8% Co, 2.5% Al, 32.4% Si, 1.5% Fe, 1.4% Cu, 1.4% Zn, and others: 5%. The tested material consisted mainly of cobalt oxide with the addition of nickel, iron, copper, and zinc. The particle size of the powdered catalyst after sieving and used for leaching was <63 µm. The 0.1–8.0 M H_2SO_4 leaching solutions were prepared using 98% H_2SO_4, p.a., Chempur, Piekary Śląskie, Poland. A 1.5% solution of HNO_3, prepared from 65% HNO_3, p.a. (Avantor Performance Materials Poland S.A., Gliwice, Poland), was applied for sample dilution for AAS analysis.

3.2. Apparatus

The content of elements in the spent catalyst was determined using an XRF analyzer (Malvern PANalytical Epsilon 1, Malvern, United Kingdom). An atomic absorption spectrometer (AAS, ContrAA 300, Analytik Jena, Jena, Germany) was used to measure the concentration of Co(II), Ni(II), Cu(II), Fe ions, and Zn(II) in an air–acetylene flame at wavelengths 240.7, 232.0, 324.8, 248.3, and 213.9 nm, respectively. Microwave plasma-atomic emission spectroscopy (4210 MP AES, Agilent, Santa Clara, CA, USA) was applied for the Al(III) determination at wavelength 396.15 nm. Appropriate dilutions were prepared to ensure that the concentration of the metal ions in the samples was in the range of the analytical curve. The concentration result was an average of three measurements.

3.3. Leaching Conditions—Design of Experiments

The optimization of the metal leaching yield was carried out by varying the parameters (factors) of the leaching process. A simple full factorial design at two levels was applied. Two factors were included in the 2^2 design, i.e., the concentration of sulfuric acid (H_2SO_4) and the leaching temperature expressed as A and B, respectively (Table 8). Using Statistica 13.3 software [37], a full factorial design was generated. The leaching efficiency of cobalt/nickel/copper/iron/zinc/aluminum obtained after leaching was the response value. Leaching experiments were carried out three times. The parameters of the experiments carried out are shown in Table 9.

Table 8. Factors and levels in the 2^2 design.

Variables	**Factors**	**Factor Levels**	
		−1	**1**
A	Molar concentration of H_2SO_4, M	0.1	8.0
B	Temperature, °C	22	70

Table 9. Parameters for the experiments carried out in 2^2 design.

No.	**A, M**	**B, °C**	**A**	**B**
1	8.0	70	+1	+1
2	0.1	70	−1	+1
3	8.0	22	+1	−1
4	0.1	22	−1	−1

Outside of the experimental plan, a series of experiments were also carried out, in which the concentration of H_2SO_4 in the range of 0.5–7.0 M was used. The experiments were carried out at an ambient temperature and at 70 °C.

3.4. Leaching Procedure

Leaching was carried out in a glass reactor (100 cm^3) with a stirrer (300 rpm). The leaching temperature was ambient (22 ± 2 °C) or 70 ± 2 °C. The solid–liquid ratio was $S/L = 1/50\ g/cm^3$ (1 g of the powdered catalyst and 50 cm^3 of the leaching solution).

The leaching efficiency (Le) of metal ions was calculated as follows:

$$\mathrm{Le} = \frac{\mathrm{m_{leach}}}{\mathrm{m_0}} \cdot 100\% \tag{8}$$

where: m_{leach}—mass of metal ions in the solution after 180 min of leaching, and m_0—mass of metal ions in the solution after mineralization.

The content of metal ions in the solution after 180 min of leaching was calculated as a ratio of the mass of metal ions in the solution after leaching (m_{leach}) to the total mass of all metal ions in the solution after leaching (m_{total}):

$$\text{Content}_i = \frac{m_{leach,i}}{m_{total}} \cdot 100\% \quad (9)$$

where "i" corresponds to a single component of the multi-component solution after leaching.

4. Conclusions

Sulfuric(VI) acid is an efficient solution for the leaching of Co(II) from spent cobalt oxide left after the preparation of an industrial catalyst. However, a high concentration of H_2SO_4 is necessary to obtain efficient leaching, as the increase in acid concentration in the leaching solution increases the amount of Co(II) leached. In addition, a positive effect of temperature was reported, and it is concluded that the leaching of Co(II) should be carried out at an elevated temperature (e.g., 70 °C). These observations have been confirmed by an ANOVA analysis, which shows that both factors, the H_2SO_4 concentration and temperature, significantly affect the leaching of Co(II) and ions of other metals. In comparison to Co leaching from other catalysts, mainly from hydrodesulfurization catalysts, the results obtained in this work are comparable (leaching efficiency near 45%). It is important from the environmental and economic points of view that the values of the leaching efficiency mentioned above were obtained without additional oxidants.

The composition of the solution after leaching with 8.0 M H_2SO_4 at 70 °C was 92.3, 0.3, 1.8, 1.9, 1.5 and 2.3% of Co(II), Ni(II), Cu(II), Fe ions, Zn(II), and Al(III), respectively. The share of Co(II) (>90%) in the solution after leaching was predominant, compared to other metal ions. As a result of the procedure proposed, a Co(II)-rich sulfate electrolyte (~4800 mg/dm^3 Co(II)), which can be applied to recover metallic cobalt by electrowinning, is proposed. However, the presence of impurities (ions of other metals) could be a problem. Therefore, prior to electrolysis, the purification of the solution would be desirable. A relatively low concentration of Co(II) in the leachate (~4800 mg/dm^3) can be a limitation for cobalt electrowinning. Therefore, further research is needed on the enrichment of the leachate with cobalt.

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

Appendix A

The concentrations of Ni(II), Cu(II), Fe ions, Zn(II), and Al(III) after 180 min of leaching at both temperatures with 0.5–7.0 M H_2SO_4 are presented in Table A1.

Table A1. The concentrations of Ni(II), Cu(II), Fe ions, Zn(II), and Al(III) after 180 min of leaching (ambient temperature or 70 °C, S/L = 1/50 g/cm^3, 0.5–7.0 M H_2SO_4).

Concentration of H_2SO_4, M	**Concentration of Metal Ions, mg/dm^3**				
	Ni(II)	**Cu(II)**	**Fe Ions**	**Zn(II)**	**Al(III)**
	Ambient Temperature				
0.5	11.8 ± 0.1	95.6 ± 0.2	72.4 ± 0.2	67.6 ± 0.1	117.6 ± 0.1
1.0	14.0 ± 0.1	94.2 ± 0.2	89.8 ± 0.2	75.6 ± 0.1	149.8 ± 0.1
2.0	14.3 ± 0.1	93.6 ± 0.2	87.4 ± 0.2	78.3 ± 0.1	129.8 ± 0.1
3.0	11.5 ± 0.1	86.6 ± 0.2	77.1 ± 0.2	67.4 ± 0.1	130.0 ± 0.1
5.0	12.3 ± 0.1	84.7 ± 0.2	86.0 ± 0.2	67.2 ± 0.1	126.2 ± 0.1
6.0	13.5 ± 0.1	95.1 ± 0.2	91.8 ± 0.2	80.0 ± 0.1	123.6 ± 0.1
7.0	13.2 ± 0.1	92.4 ± 0.2	83.4 ± 0.2	72.0 ± 0.1	118.6 ± 0.1
	70 °C				
0.5	13.5 ± 0.1	91.2 ± 0.2	88.4 ± 0.2	76.8 ± 0.1	110.6 ± 0.1
1.0	15.6 ± 0.1	99.1 ± 0.2	122.8 ± 0.2	81.5 ± 0.1	112.4 ± 0.1
2.0	12.7 ± 0.1	98.4 ± 0.2	114.4 ± 0.2	73.9 ± 0.1	106.6 ± 0.1
3.0	13.9 ± 0.1	99.3 ± 0.2	111.4 ± 0.2	74.8 ± 0.1	102.2 ± 0.1
5.0	13.6 ± 0.1	95.4 ± 0.2	112.6 ± 0.2	74.4 ± 0.1	107.8 ± 0.1
6.0	14.8 ± 0.1	95.5 ± 0.2	106.3 ± 0.2	78.9 ± 0.1	106.4 ± 0.1
7.0	13.4 ± 0.1	86.4 ± 0.2	81.1 ± 0.2	67.8 ± 0.1	106.5 ± 0.1

Leaching efficiencies of Co(II), Ni(II), Cu(II), Fe ions, Zn(II), and Al(III) after 180 min of leaching with 0.5–7.0 M H_2SO_4 at both temperatures are presented in Table A2.

Table A2. Leaching efficiency of Co(II), Ni(II), Cu(II), Fe ions, Zn(II), and Al(III) after 180 min of leaching (ambient temperature and 70 °C, S/L = 1/50 g/cm^3, concentration of H_2SO_4 was 0.5–7.0 M).

Concentration of H_2SO_4, M	**Le, %**					
	Co(II)	**Ni(II)**	**Cu(II)**	**Fe ions**	**Zn(II)**	**Al(III)**
	Ambient Temperature					
0.5	22.9	26.6	34.2	17.6	20.7	19.8
1.0	24.4	31.6	33.7	21.8	23.1	25.2
2.0	24.7	32.1	33.5	21.2	23.9	21.8
3.0	24.2	25.8	30.9	18.7	20.6	21.9
5.0	27.0	27.7	30.3	20.9	20.5	21.2
6.0	28.7	30.4	34.0	22.3	24.4	20.8
7.0	31.2	29.7	33.0	20.2	22.0	19.9
	70 °C					
0.5	25.5	30.3	32.6	21.5	23.5	18.6
1.0	27.0	35.1	35.5	29.8	24.9	18.9
2.0	28.2	28.6	35.2	27.8	22.6	17.9
3.0	32.7	31.2	35.5	27.0	22.8	17.2
5.0	36.8	30.6	34.1	27.3	22.7	18.4
6.0	35.8	33.2	34.1	25.8	24.1	17.9
7.0	36.2	30.1	30.9	19.7	20.7	17.9

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