

Recovery of cobalt and WC from cemented carbide scrap-Part II: Recovery of submicron cobalt powder from the leach solution

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In this study, it is aimed to treat cemented carbide scrap (hard metal WC-Co) by nitric acidic leaching, followed by the precipitating of cobalt hydroxide, and finally obtaining a submicron size pure cobalt metal powder by a thermal breakdown and the hydrogen reduction of this hydroxide in a horizontal tube furnace in a process step. A comparison of different precipitating reagents and optimization of the precipitation parameters are also conducted along with a search for the possible existence of an environment-friendly and economic process. According to the results obtained, it is possible to dissolve cobalt with high efficiencies (min. 91.5%) via HNO₃ leaching of cemented carbide scrap. The optimum leaching conditions were found to be: <90 µm, 25 °C, 2 h, 0.5 M HNO₃, 900 rpm and 1/10 solid/liquid ratio. Moreover, it has been found that cobalt could be precipitated with an efficiency of >98% in the form of hydroxide by addition of an alkaline reagent like NaOH. Cobalt hydroxide is transformed into a pure cobalt powder (99.7 %) by a thermal breakdown process (>300°C, 0.5 h, with Argon) and by a reduction with hydrogen (800 °C) under controlled conditions in 1.5 h to yield a submicron cobalt powder. The metallic Co-powder obtained has a purity of 99.7 % Co and BET specific surface area of 0.37 m²/g.

Keywords: Cemented Carbide Scrap, Acidic Leaching, Precipitation, Calcination, H₂-Reduction, Co-powder

Rückgewinnung von Kobalt Pulver und Wolframkarbid aus Hartmetallschrotten – Teil II: Gewinnung von Submikron Co-Pulver aus Laugungslösung

Das Ziel der vorliegenden Arbeit ist die Gewinnung von Kobalt submikron-Pulver aus Hartmetallschrott (WC-Co) durch saure Laugung. Kobalt wird mit HNO₃ gelaut und anschließend als Kobalt-Hydroxid gefällt, welches durch thermische Behandlung und H₂-Reduktion, die in einem Arbeitsschritt stattfinden, in einem horizontalen Rohrofen zu reinem submikron Kobaltpulver geführt. Verschiedene Fällungs-Reaktanten wurden verglichen, um die Optimierung der Parameter für die Fällung im Rahmen eines umweltfreundlichen und ökonomischen Prozesses zu simulieren. Gemäß der Versuchsergebnisse kann Kobalt mit einem Ausbringen von min. 91,5 % durch Laugung von Hartmetallschrott mit HNO₃ gelöst werden. Optimale Laugungsbedingungen herrschen bei: < 90 µm, 25° C, 2 Stunden, 0,5 M HNO₃, einer Rührgeschwindigkeit von 900 U/min und einem Fest-Flüssig-Mischverhältnis von 1 zu 10. Weiterhin wurde herausgefunden, dass Kobalt in Form von Hydroxid durch die Zugabe eines alkalischen Reaktanten, wie z.B. NaOH, mit einer Effizienz von >97 % gefällt werden kann. Kobalt-Hydroxid kann durch thermische Spaltung (>300°C, 0.5 h) und H₂ Reduktion (800 °C) unter kontrollierten Bedingungen innerhalb von 1,5 Stunden zu reinem Kobalt-Pulver umgewandelt werden, um Kobalt-Pulver in submikron-Größe zu erhalten. Das metallische Co-Pulver verfügt über einen Reinheitsgrad von 99.7 % Co und eine spezifische Oberfläche von 0.37 m²/g.

Schlüsselwörter: Hartmetallschrott, Saure Laugung, Fällung, Kalzinieren, H₂-Reduktion, Co-Pulver

Récupération de cobalt et WC (carbure de tungstène) à partir de chute de carbure cimenté Partie II: Récupération de cobalt-poudre submicronique par lixiviation acide

Recuperación de cobalto y carburo de tungsteno a partir de chatarra de carburos cementados. Parte II: Recuperación de polvos submicranos de cobalto presentes en la solución de lixiviación

1 Introduction

Cobalt is a metal of high economic and strategic importance, largely because of its wide range of high performance applications and dwindling supplies. Cobalt is used mainly in specialist chemicals (for rechargeable batteries), super alloys, diamond tools, hard metal and magnets. Cobalt can be extracted from concentrates and occasionally directly from the ore itself by hydrometallurgical, pyrometallurgical, and electrochemical processes. Although most processes of extraction are based on hydrometallurgy, cobalt concentrates, mattes, and alloys have to be reduced to metal by pyrometallurgical methods. Cobalt is typically produced as a byproduct of more abundant metals like Nickel. Cobalt production (refined cobalt in the form of metal and chemicals) amounted to 24.471 tonnes in 1997. However, 25.192 tonnes of refined cobalt from primary routes were actually supplied to western world markets in the same year. In 1997, the global demand for cobalt reached 31.400 tonnes. The difference between refined supply and demand was filled by lower grade and recycled materials that were converted mainly into chemicals. Cobalt consumption as a function of end use share is estimated for super alloys to 26.0 %, for hard materials to 14.3 %, for colors to 12 %, for magnets to 9.0 %, for tire adhesives to 9.4 %, for catalysts to 8.5 %, for batteries to 7.5 %, for hard facing/other alloys to 7.0 %, and for sulfates to 5.5 %. In 2002, the global demand for cobalt reached 39.000 t and 40.000 t in 2003, with a forecast of a further increase to over 42.000 t in 2004. Figure 1 shows World consumption cobalt usage by end use. The main categories of secondary cobalt are chemicals, super alloys, cemented carbides and magnets. The chemical sector is, and will remain, the largest end-use sector for the next years. Specifically, chemicals used in rechargeable batteries (especially Li-Ion and NiMH) are having a significant impact on the overall consumption of cobalt in this category [1-4].

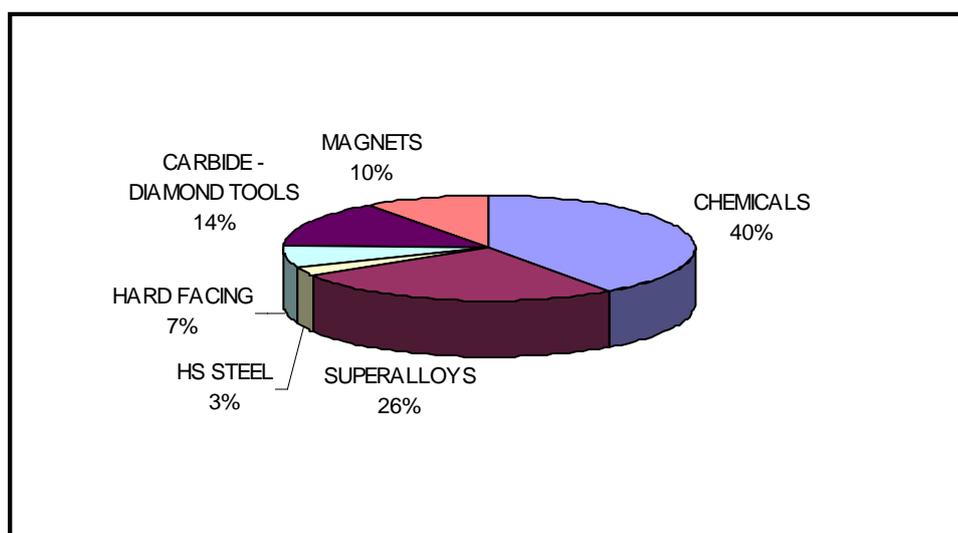


Fig. 1: World consumption of cobalt by end use [2,3]

One of the important uses of cobalt is a bonding agent in cemented carbides that are used extensively as cutting tools for metals, rocks and other high strength materials. No suitable

substitute has been found for cobalt as a cementing agent for carbides. The majority of cemented carbides are based on WC and Co and the present publication series is focussed to this system. The most common used hard metals contain 2-30 % cobalt. The properties of cemented carbides are controlled by the amount of cobalt added as well as type and particle size of the carbides used. It is evident that the processing of nanostructured WC powders, with cobalt as a binder phase, will lead to materials of superior hardness and a refined microstructure. Machine tools, dies, high-pressure valves for the oil field industry, thin hard metal wires, drills and disc-type slitting knives for the computer industry are examples of WC-Co applications. WC is the most important carbide for this application, with a world market for the tungsten carbide-cobalt (WC-Co) composite powders estimated to be at 20.000 t each year. Even though the demand for WC in cutting tool industries is decreasing, its application in the field of catalysis industries is very promising. Owing to economic and technological constraints, production of high quality powders (submicron, high purity etc.) for hi-tech applications constantly impose fresh demands on further investigations of the production routes [5-11].

The main sources of secondary (recycling) cobalt are Ni-based super alloys, catalysts, magnets, and cemented carbides. The recycling of hard-metal scrap has reached significance as about a third of the cobalt consumption in this sector arises from recycled cobalt. Most scrap materials are richer in cobalt than even ore concentrates. A typical cobalt concentrate assays as follows: 1.76 % Co, 9.4 % As, 22.9 % Fe. The grade of the cobalt in scraps range from 2-30 %. In recent years, stringent environmental controls and resource conservation policies have led to renewed interest in developing cemented carbide recycling techniques that are not only economically viable but also ecologically acceptable. The existing process alternatives for hard metal recycling (Fig. 2) can be divided into three different principles [8,9].

- A. Direct conversion into graded powder ready for pressing and resintering
This can only be done with sorted hard scrap. The most important processes are the so called "Zinc Process" and the "Cold-Stream Process".
- B. Leaving the carbide mixtures and chemistries as they are, but removing the binder chemically is a second way of hard metal recycling.
- C. All contaminated scraps-either soft or hard- are treated by a chemical conversion process "total leach" to recover virgin powders of the hard metal constituents [oxidation, pressure leaching, filtration, precipitation steps for purification, APW-crystallization, conventional WC-Powder].

Selective cobalt leaching from cemented carbide scrap (principle B) offers the potential of a environmental friendly management in view of its lower energy consumption and environmental impact due to the reduced number of process steps. In this study a process has been developed for the recycling of cobalt and WC from cemented scrap carbides. Cobalt is recovered in form of powder besides a carbide mix powder (WC, TiC) which today are the most important products for powder metallurgy. Three basic process steps are needed for cobalt powder production:

- Acidic leaching
- Precipitation
- Calcination and H₂-reduction

The most important advantages of dissolving cobalt in acidic solutions is its environment-friendliness and having less process steps, as compared to the classical processes, where the cemented carbide scraps are treated in furnaces or dissolved by NaOH in autoclaves.

2 Experimental

The leach solution of nitric acid leaching of cemented tungsten carbide scrap (details see Part I) was used as the starting material for this research [12]. Leaching experiments were carried out in a glass reactor with 0.5 l capacity. Precipitation experiments were conducted with an Ika-Werk brand heater-magnetic stirrer, regular glassware and a contact thermometer. Precipitation experiments were conducted at different temperatures (25-55 °C) and pH (7-11) on the leach solutions. A WTW brand pH meter was used for measuring the pH values of solutions. A 2 M NaOH-solution was slowly added to the stirred leach solution until a desired equilibrium pH was achieved. The solution was agitated at the desired pH for 30 min. The precipitate was then separated from the solution by filtration. After precipitation a two step processing (calcination at 300 °C and H₂-reduction at 800 °C) has been used to directly synthesize submicron cobalt powder. Table 1 summarizes the conditions for precipitation, calcination and hydrogen reduction adapted in the present work.

Table 1: Experimental conditions

for precipitation				
T (°C)	pH	T (min)	NaOH	starting material
25-55	7-11	30	2 M	Co(NO ₃) ₂ solution
for calcination and hydrogen reduction				
300		30 min	with Argon	Co(OH) ₂
700-900		90 min	with Hydrogen	

A horizontal tube furnace with an ID of 25 mm (Ströhlein), a quartz tube (700 mm length and 20 mm diameter) and alumina boats are used for the cobalt powder production from cobalt hydroxide by the hydrogen reduction technique. The surface area of the cobalt powder was measured by BET equipment (Flow Sorb II 2300). An X-ray diffractometer (Siemens D 5000) and a scanning electron microscope (JEOL, JSM T330) were utilized for the characterization of the product. All chemicals used in the experiments were analytical grade (Merck). Figure 2 displays the experimental setup of recovery submicron cobalt powder from powderized cemented carbide scrap.



Leaching

Precipitation

**Calcination / Reduction and
Co-Powder at 800 °C**

Fig. 2: Experimental setup

3 Results and Discussion

3.1 Leaching

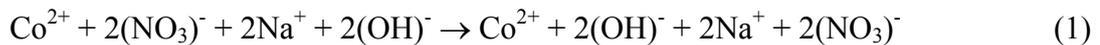
Leaching of cobalt from powderized cemented carbide scrap in nitric acid solution is a function of temperature, time, concentration of the nitric acid solution, stirring rate and solid/liquid ratios. The optimum leaching conditions were found to be as: <90 μm , 25 $^{\circ}\text{C}$, 2h, 0.5 M HNO_3 , 900 min^{-1} stirring rate and solid/liquid ratio:1/10. According to the results obtained, it was possible to dissolve cobalt with high efficiencies (91.5%) via HNO_3 leaching of cemented carbide scrap [12]. The filtration following the leaching process is significantly easy. The composition of the homogenized leach solution for the precipitation experiments (analysed by ICP Spectroflame Modula EOP) is shown in Table 2, which indicates that Fe and Ni are two major impurities. The cobalt is the major component to be recovered. The leach residue was washed by distilled water.

Table 2: Chemical composition of leach solution

The leach solution	g/l
Co	4.63
Fe	1.59
Ni	0.36
Ti, W	<0.0005

3.2 Precipitation of cobalt hydroxide

A precipitation process can be used to separate from others, either for the purpose of removing impurities or for the recovery from solution. The selective precipitation of metal hydroxides by appropriate control of the solution pH theoretically feasible. A strong alkaline such as sodium hydroxide is often used as a precipitating agent for metal hydroxides. Cobalt recovery from solutions with hydrometallurgical techniques is strongly dependent on the process parameters such as pH of the solution, temperature, type and concentrations of the reagent. Cobalt ions dissolved in a nitric acidic leach are selectively precipitated by the addition of 2 M NaOH -solution, according to Eq. (1).



The theoretical background of hydroxide precipitation can be explained by the help of a Pourbaix diagram. As Fig. 3 shows Cobalt hydroxide [$\text{Co}(\text{OH})_2$] precipitation is possible above pH 5 at 55 $^{\circ}\text{C}$.

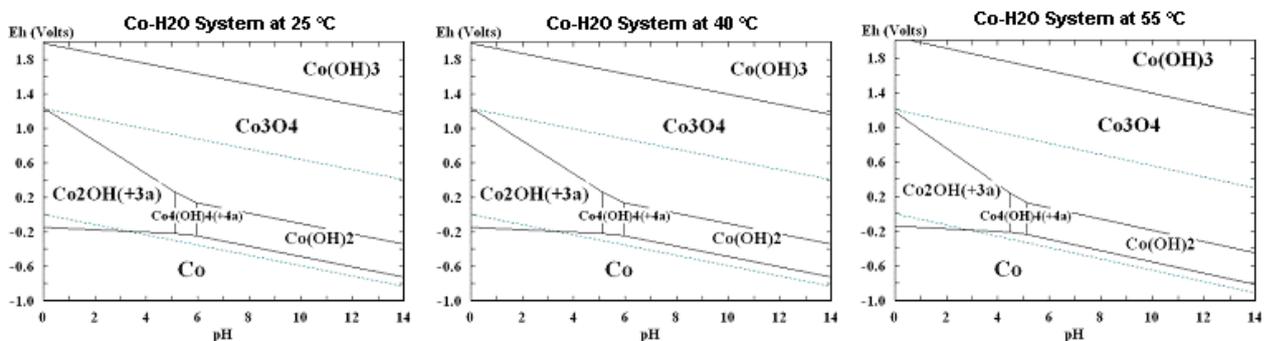


Fig. 3: Potential-pH equilibrium diagrams for the system cobalt-water at 25, 40 and 55 $^{\circ}\text{C}$.

After addition of sodium ions the leach solution cobalt hydroxide starts to precipitate immediately (see Fig. 4.a and b).

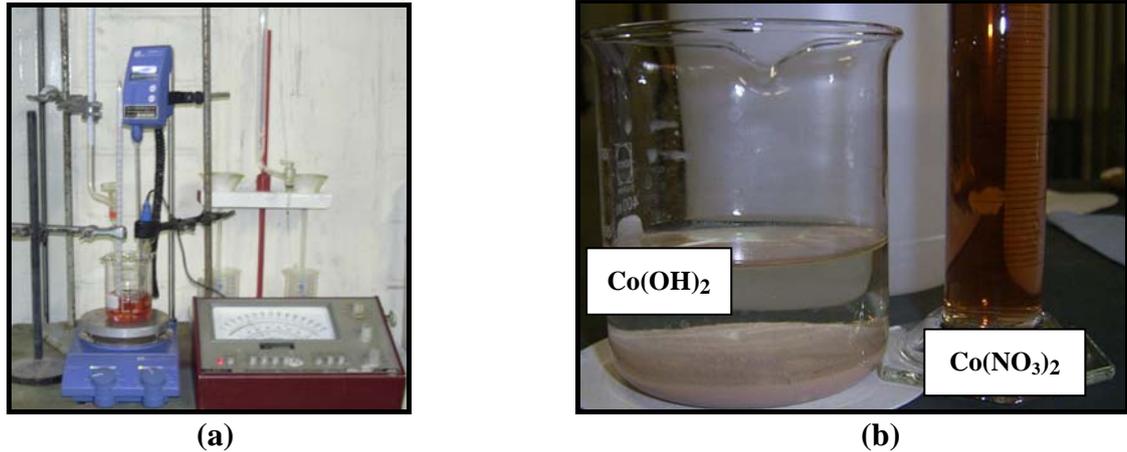


Fig. 4: a) The precipitation reactor and b) Co(OH)_2 -filtrate

Iron and nickel also found in the leach solution in significant concentrations were preliminaries precipitated as hydroxide Fe(OH)_3 and Ni(OH)_2 in nitric acid solution in the 2-5 pH range. The precipitation efficiency increases with increase in pH [13]. It started just above 2 and the precipitate was then separated from the solution by filtration in order to receive a pure Co-solution.

3.2.1 Effect of pH and temperature on precipitation efficiency

Precipitation experiments were conducted at different pH and temperatures using similar leach solutions (100 ml). According to the Pourbaix diagram of the Cobalt-Water system Co(OH)_2 was precipitated between pH 7-11. The results are listed in Table 3.

Table 3: Results of precipitation experiments obtained at different pH and temperatures (2 M NaOH, in 30 minutes)

pH	Temp.	Concentration		
		Co (mg/l)	Fe (mg/l)	Ni (mg/l)
Initial solution (after Fe/Ni precipitation)		4600	10	8
Final solution		Co	Fe	Ni
7	25 °C	2075	8,7	3,2
	40 °C	795	5.5	1.5
	55 °C	470	2.2	1.2
9	25 °C	630	2.7	1.2
	40 °C	120	2.5	1.0
	55 °C	74	2.3	1.0
11	25 °C	2.0	2.0	1.0
	40 °C	1.0	1.0	1.0
	55 °C	<1.0	<1.0	<1.0

As seen from Table 3, the metal ion concentration after precipitation decreases with increasing pH and temperature. The optimum hydroxide precipitation conditions are obtained at pH=11 and 55°C (see Table 4). The precipitation efficiency of Co is over 98 % at a temperature 55 °C and pH 11 respectively. Huang et al.[14] have been shown that the increased temperature and pH can influence the increase of precipitation efficiency. Temperature of solution is important for precipitation processes. Increasing temperature from 25 °C to 55 °C increases the kinetic

energy of particles and thus it increases the precipitation efficiency. The colors of the hydroxide vary from pink to light pink (see Fig. 4), depending on the precipitation conditions. It is commonly used as a starting material in the synthesis of cobalt chemicals.

Table 4: Optimum hydroxide precipitations conditions

T (°C)	pH	T (min)	NaOH	Precipitation efficiency (%)		
				Co	Fe	Ni
55	11	30	2 M	>98	>98	>98

Figure 5 displays the SEM micrograph of cobalt hydroxide produced at 55 °C and pH 11. The cobalt hydroxide obtained displays a spongy and porous character.

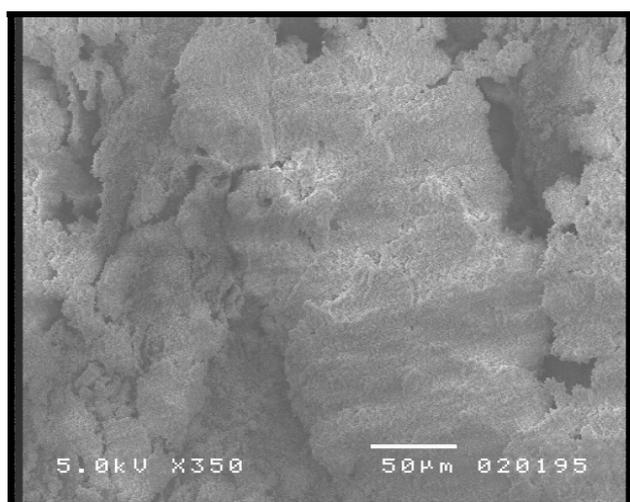
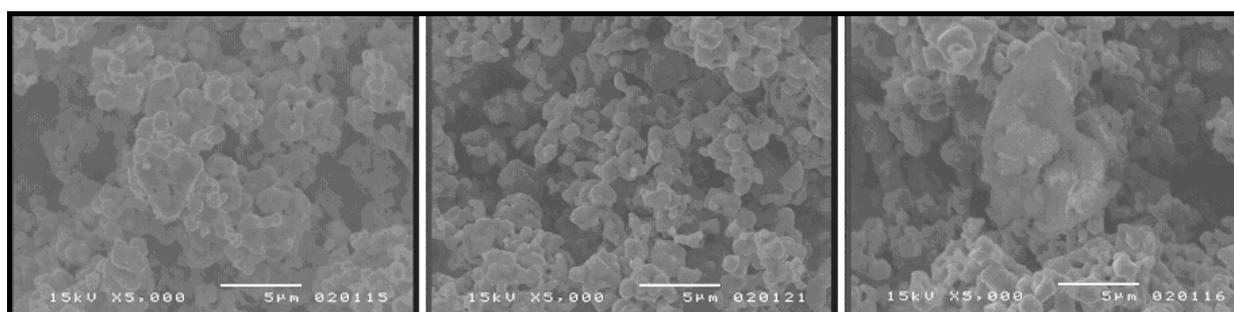


Fig. 5: SEM micrograph of the cobalt hydroxide obtained at 55 °C and pH 11

3.3 Calcining and Hydrogen reduction

Cobalt powder can be produced by a number of methods, but those of industrial importance involve the thermal hydrogen reduction of oxides, the pyrolysis of carboxylates, and the reduction of cobalt ions in aqueous solution with hydrogen under pressure. The cobalt compound, received after precipitation from the solution is cobalt hydroxide, which can be transformed into cobalt powder by a thermal calcining process carried out at > 300 °C under Argon followed by a reduction process. This is carried out under hydrogen gas within a temperature range of 700 to 900°C. Thermal calcining and the reduction period lasts 2 hours. The weight loss ratios vary between 5.9 and 9.7 %. The hydrogen reduction technique is selected to benefit from the advantageous effects of utilizing submicron sized powders during the industrial manufacturing of final products through powder metallurgy methods. SEM micrographs (Fig. 6) prove that the cobalt powder obtained was mainly submicron in size. With increasing temperatures the grain size getting enlarged.



700 °C

800 °C

900 °C

Fig. 6: SEM micrographs of the cobalt powder

During the calcination and reduction, micron size particles of cobalt powder started to agglomerate with increasing reduction temperature from 700 to 900 °C at a submicron scale of 0.3-5 µm. The slightly agglomerated particles exhibit spherical morphology. The chemical composition of the cobalt powder is given in Table 5.

Table 5: Chemical analysis of the cobalt powder produced at 800 °C.

Wt. %	Co	Fe	Ni	Average Particle Size	BET - Surface
	99.7	0.04	0.02	0.3 - 5 µm	0.37 m ² /g

Cobalt powder produced is suitable for powder metallurgy applications in terms of both particle size distribution and chemical composition, which can be seen by comparing it with typical specifications also shown in table 6.

Table 6: Typical properties of reduced cobalt powders for powder metallurgy [6]

wt. %	Co	Fe	Ni	Average Particle Size	Apparent Density
	99.6	0.08	0.08	5 µm	1.8 g/cm ³

4. Conclusions

This technique represents an alternative process to the classical recycling techniques. Using optimum leaching conditions as: <90 µm, 25°C, 2 hours of leaching period, 0.5 M, 900 min⁻¹ and solid/liquid ratio: 1/10. Cobalt can be precipitated by the additions of NaOH with yields >97 %. This hydroxide can be transformed into submicron, pure cobalt powder through a thermal calcining operation carried out at > 300°C under Argon and a hydrogen reduction technique. The average particle size of cobalt powder increases with increasing calcining and reduction temperature. Not only the reduction but also the precipitation conditions and the calcining affect the particle size of cobalt powder. A total of 2 h reduction time is required (0.5 h at 300°C, and 1.5 h at 800°C) for the reduction of Co(OH)₂ to cobalt powder. Cobalt powder produced can be readily used in powder metallurgy applications with its 99.7 % purity and surface area of 0.37 m²/g.

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