Recovery of submicron cobalt-powder by acidic leaching of cemented carbide scrap

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Abstract

This study aims on the treatment of 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 thermal breakdown and the reduction of this hydroxide in a horizontal tube furnace using hydrogen gas. According to the results obtained, it is possible to dissolve cobalt with high efficiencies (min. 91.5%) via HNO_3 leaching from cemented carbide scrap. Effective leaching conditions were found to be: <90 μm, 25 °C, 2 h, 0.5 M HNO_3, 900 rpm and 1/10 solid/liquid ratio. Moreover, it has been found that cobalt could be precipitated with an efficiency of > 97 % in the form of hydroxide by addition of an alkaline reagent like NaOH. Cobalt hydroxide was transformed into a cobalt powder (99.7 %) by a simple thermal breakdown process (>300°C, 0.5 h, with Argon) and by a reduction with hydrogen under controlled conditions in 1.5 h to yield a sub-micron-structure. Weight loss ratios in the reduction process vary between 5.9 and 9.7 % at the end of a 2.0 hour calcination and reduction step. The thermal breakdown and reduction kinetics of the cobalt hydroxide, amount of impurities it contains, and its morphology have significant effects on the properties of cobalt-powder. The metallic Co-powder obtained has a purity of 99.7 % Co and specific surface area of 0.37 m^2 / g. The characterization studies of the WC leach residue aiming for the re-utilization possibilities in the Hard Metal Industry (or Powder Metallurgy), revealed that it has a density of 11.9 g/cm^3, and a BET value of 1.08 m^2/g.

1   Introduction

Fine metallic powders with high purity offer new physical and mechanical properties. Today, cobalt is considered as one of the metals of high economic value and strategic importance, and it is widely used in electrochemical, hard metals, magnetic and catalytic materials industries. The increasing demand for metals in the world has required intensive studies for the extraction of metals from low-grade ores and/or secondary resources. Most scrap materials are richer in cobalt than even ore concentrates. Extraction of cobalt can be performed from secondary resources like chemicals (for rechargeable batteries), super alloys, cemented carbides, and magnets. "Cemented carbides", often called "Hard Metals" are a range of very hard, refractory, wear-resistant materials made by powder metallurgical techniques (sintering). These materials have found wide usage in applications such as cutting tool inserts (about 50-60 %), dies, nozzles, valve components, etc., where severe wear and high temperature properties are required. The recycling of hard-metal scrap has reached significance as about a third of the cobalt consumption in this sector arises from recycled cobalt. When the tools and components are scrapped, they are collected with the purpose of recovering the tungsten and cobalt in the light of their strategic importance. The $2 billion worldwide cemented carbide industry generates large quantities of scrap due to the rejected parts at various stages of production and the worn out cutting tools. Numerous recycling processes have been developed that can be classified into different categories. The first group involves chemical modification of the component metals into intermediate products, which are then processed to obtain pure metals. The second group involves removal of the binding medium from the matrix, leaving behind a finely divided tungsten carbide, which can be recycled to fabricate new tools. Today, many contaminated scraps - either soft or hard- are treated by chemical conversion processes [oxidation, pressure digestion (NaOH), filtration, purification, conventional W and WC powder manufacturing route] to gain back virgin powders of the hard metal constituents. The "Zinc melt" and the "Cold-Stream" processes are also popular methods to recycle cemented carbide. Regarding the "Zinc melt" process, the binding metal (cobalt) reacts with high purity zinc (99.995%) during the cemented carbide recovery operation. The energy consumption is therefore high; about 4000 to 6000 kWh is required for one ton of tungsten carbide scrap. The cycle time of the complete zinc process is 24 hours. The "Cold-Stream" process is a mechanical method where cemented carbide scrap is transported by a high velocity air stream (>1000 km/h) to hit on a cemented tungsten carbide plate. Nitric acid is used to dissolve the binding medium (anodic dissolution of cobalt) at a current density of 2-10 A kg^{-1} of the scrap (an electrochemical process) [1-12]. Furthermore, several hydrometallurgical processes have been developed and used to extract cobalt from various sources. Cobalt leaching from cemented carbide scrap is a hydrometallurgical method for cobalt recovery and offers the potential of an environment-friendly management. Selective leaching is a potential alternative in view of its lower energy consumption and environmental impact.

In this study, a process has been developed for the recycling of cobalt from cemented carbide scrap. The process to recover cobalt involves three steps: acidic leaching, precipitation, thermaldecomposition and H_2-reduction.

2   Experimental

2.1. Materials

Experiments were carried out with powderized cemented carbide scrap. The chemical composition of the cemented tungsten carbide scrap powder is given in Table 1.

Table 1: Chemical composition (wt%) of the cemented tungsten carbide scrap powder (-90μm).

W	Co	C	Ti	Fe	Nb	Ni
75.86	8.14	6.07	4.18	3.40	1.35	1.00

X-ray analysis of the raw material is given in Fig. 1.
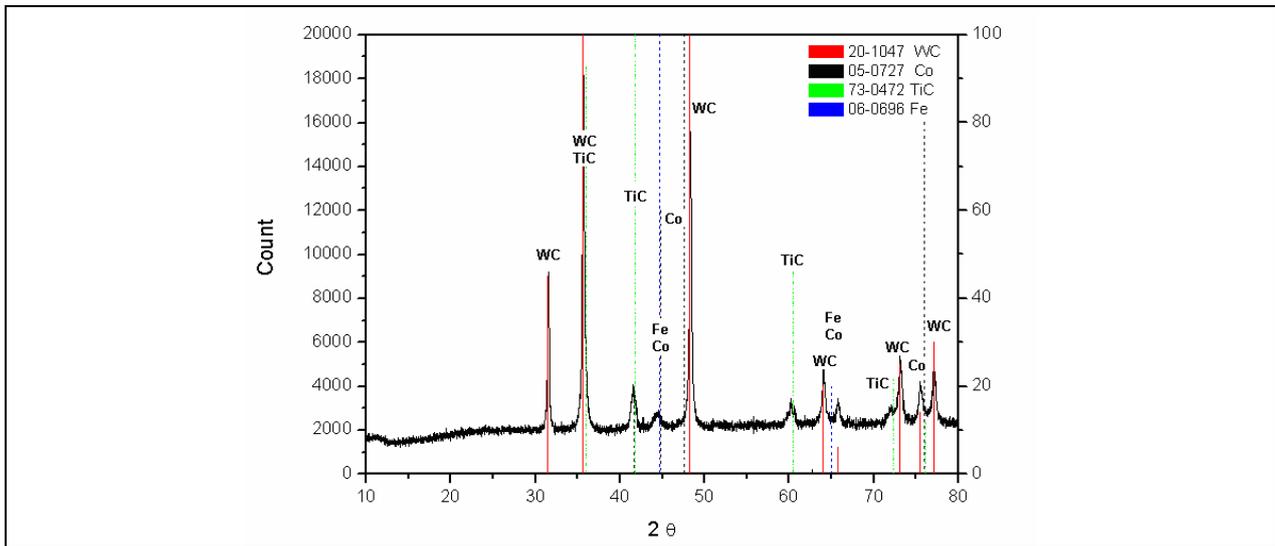
Figure 1: X-ray analysis of cemented carbide scrap powder (-90μm).

By the X-ray diffractometer, it was found that the structure of cemented carbide scrap is WC, TiC, and Co.

2.2. Experimental procedure

Cemented tungsten carbide scrap was ground in a vibrating mill for 15 minutes. Screening of the ground material was conducted in a Retzsch brand sieve. Leaching experiments were carried out in a three-neck glass reactor with 0.5 l capacity, heated by a thermostatically controlled heater (Heraeus). The mixture was stirred from the top with a teflon-plated propeller, which was hooked on to a mixer (Ika-Werk RW-20) with adjustable speed and stirring direction. A spiral condenser was also utilized to return evaporation losses to the system. The ground cemented carbide scrap powder was added into the agitated nitric acid solution at the required temperature. Samples of the solution were taken in a thirty minutes interval. All the samples were filtered and analyzed by ICP (Spectroflame Modula EOP). Carbon content of cemented carbide scrap was determined by using Leco-CS 400 analyzer. 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 H_2-reduction at 800 °C) has been used to directly synthesize submicron cobalt powder. 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 and 5410) 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.
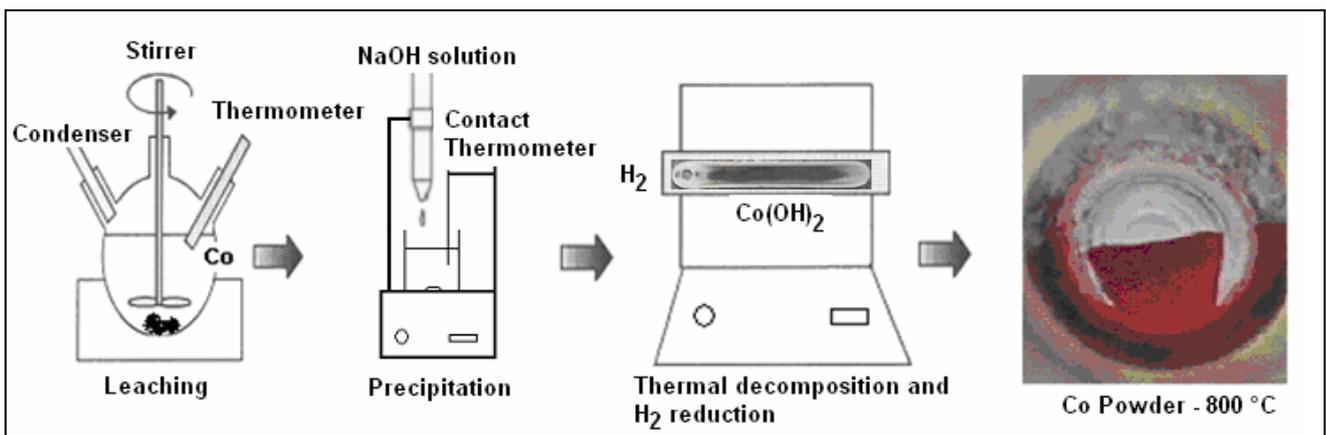
Figure 2: Schematics of the experimental apparatus for the synthesis of cobalt powder.

3. Results and discussion

3.1 Leaching

3.1.1. Effect of leaching temperature

The temperature effect was examined in the range of 25-70°C under the standard conditions of: -90µm particle size, 0.5 M HNO_3, 2h, 900 rpm, and 1/10 solid/liquid ratio. Figure 2 shows the effect of temperature on the dissolution of cobalt in the HNO_3 and H_2O system. As seen from Fig. 3, cobalt solubility decreases from 91.5% to 78.2% between the temperatures of 25 and 70°C.
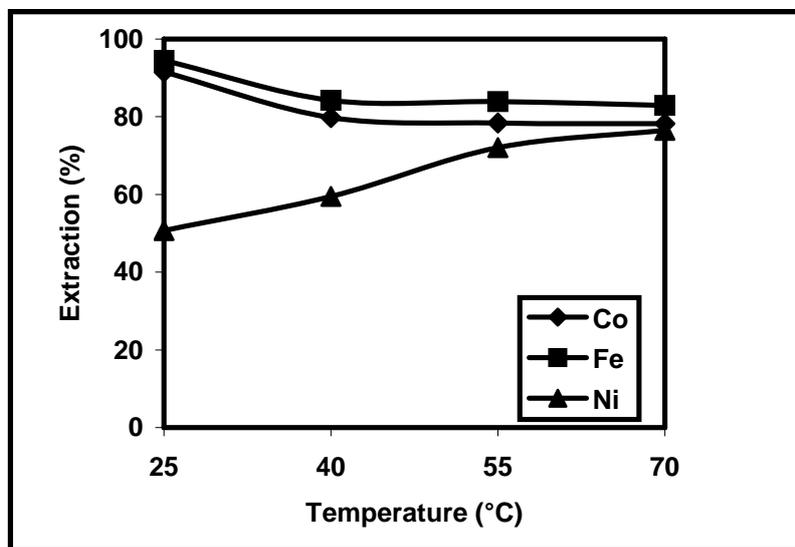
Figure 3: Effect of temperature on the dissolution of cobalt and associated elements [-90µm, 2h, 0.5 M HNO_3, 900 rpm, and S/L: 1/10].

The effect of temperature on cobalt leaching from cemented carbide scrap is shown in Figure 4. The cobalt extraction increases with increasing leaching time. The maximum value of cobalt extraction amounts to 91.5% at 25°C and a leaching time of 120 min.
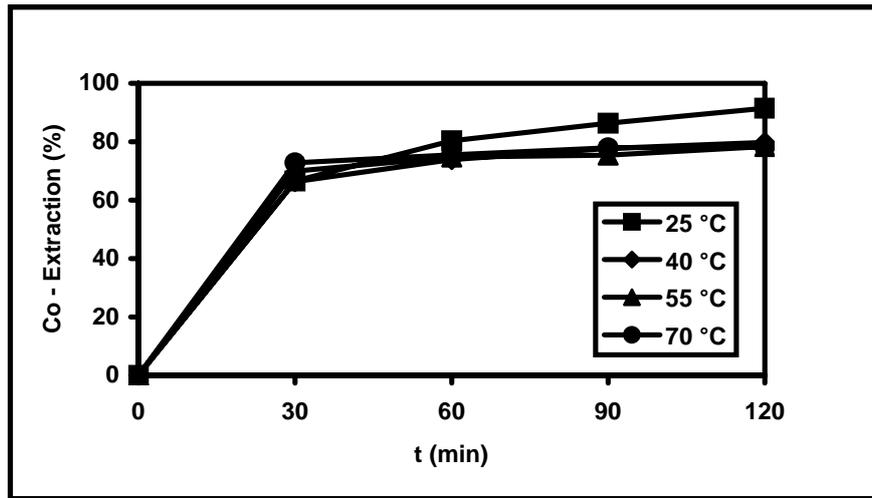
Figure 4: Effect of temperature on cobalt leaching kinetics [-90 μm, 0.5 M HNO_3, 900 rpm and S/L: 1/10].

The leach residue was washed by distilled water. X-ray analysis of the leach residue (for the optimum leaching conditions) is given in Figure 5. While the main structure shows typical WC and TiC characteristic, some cobalt peaks observed in X-ray analysis indicate that additional grinding might be necessary in order to liberate all the cobalt present in the scrap.
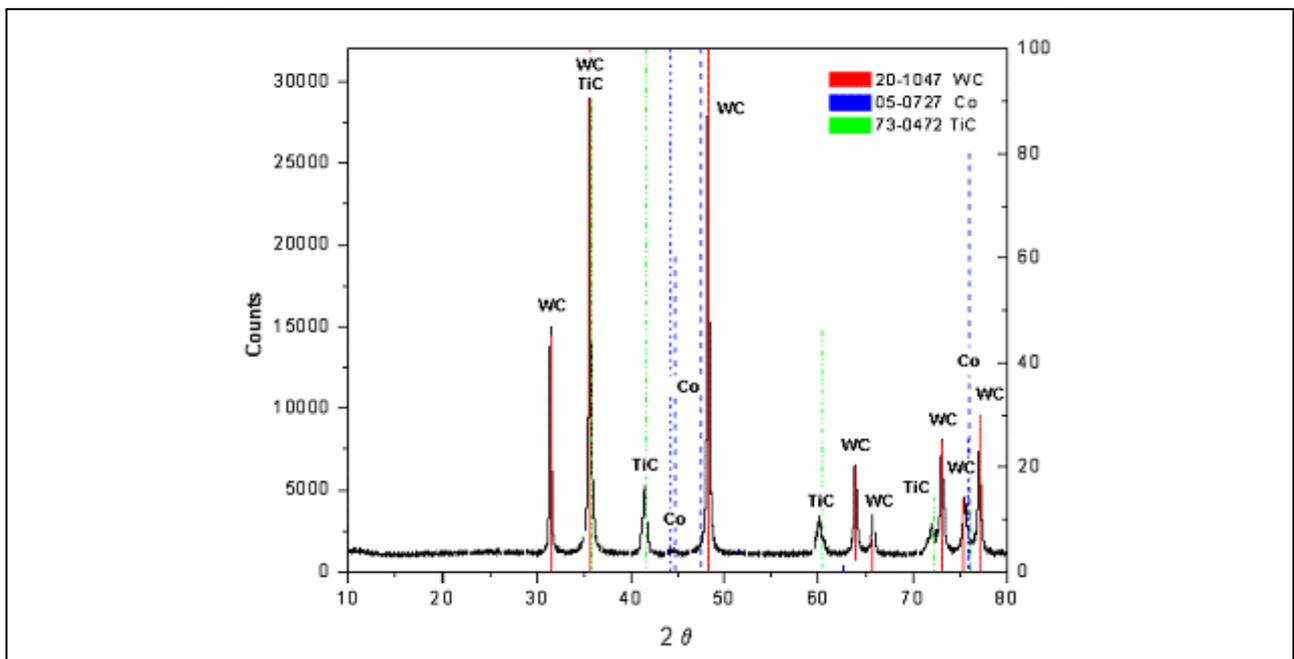
Figure 5: X-ray analysis of the leach residue (the optimum leaching conditions).

Figure 5 indicates that the residue mainly consists of WC and TiC. The physical properties of the leach residue are given in Table 2.

Table 2: The physical properties of the leach residue.

Grain Size	Density	Surface area
-90 μm	11.9 g/cm^3	1.08 m^2/g

The characterization studies, conducted on WC leach residue aiming for the re-utilization possibilities in Hard Metal Industry (or Powder Metallurgy), revealed that it has a density of 11.9 g/cm^3, and a BET value of 1.08 m^2/g. These results were in accordance with the literature values of WC [5]. It is well known that WC–Co cemented carbide has higher strength and hardness with decreasing of WC grain size.

3.1.2. Effect of reaction time

The highest cobalt efficiency (91.5%) was obtained after a leaching period of 2 h (Figure 6). Iron, on the other hand, dissolves within the first hour of leaching with 90% efficiency and shows similar dissolution trend of cobalt for the rest of the leaching. This result shows that the reaction period and rate depending on the liberation rate of the particles in ground cemented carbide scrap. In practice, 120 min of leaching time was found to be the optimum. Extended leaching periods (over 120 min) seem to increase the efficiency for cobalt, iron, and nickel, only insignificantly.
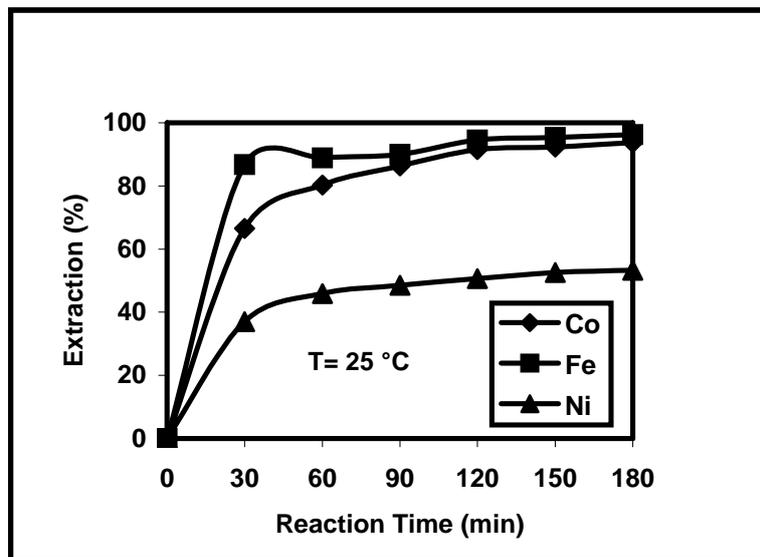
Figure 6: Effect of leaching time on the dissolution of cobalt and associated elements [-90μm, 25°C, 0.5 M HNO$_3$, 900 rpm, and S/L: 1/10].

3.1.3. Effect of initial acid concentration

Figure 7 displays the effect of acid concentration on the dissolution of cobalt at 25°C. Various experiments were carried out by changing the HNO$_3$ concentration from 0.5 M to 1.5 M. At 0.5 M

HNO_3 concentration, 91.5% cobalt extraction was obtained in 120 min, as shown in Fig. 7. Increasing the acid concentration from 0.5 M to 1.5 M caused the dissolution efficiency of iron to decrease from 94.5% to 90.0%. On the other hand, nickel extraction increased with increasing HNO_3 concentration.
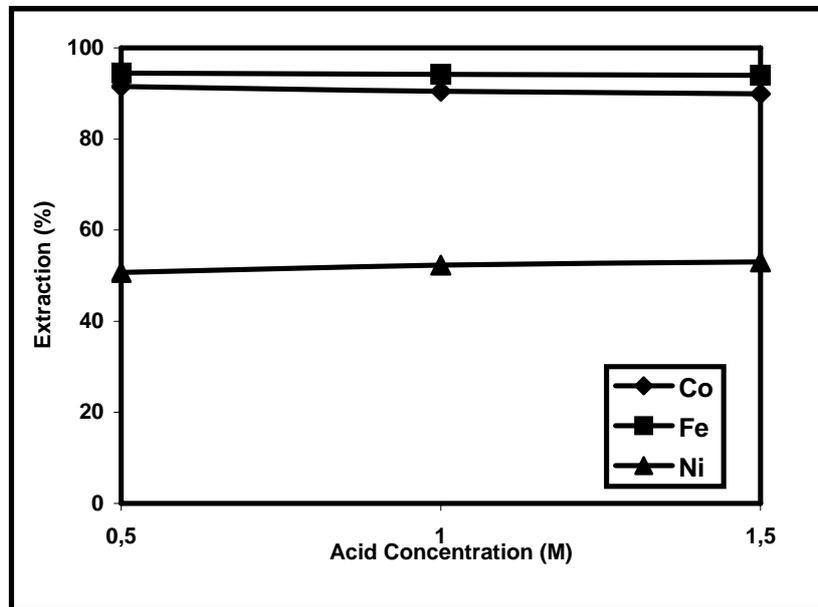
Figure 7: The effect of acid concentration on the dissolution of cobalt and associated elements [-90μm, 25°C, 2h, 900 rpm, and S/L: 1/10].

3.1.4. Effect of stirring speed

The effect of the stirring speed was studied under the conditions of -90μm particle size, 25°C, 0.5 M HNO_3, 2h, and 1/10 solid/liquid ratio. The results show that the leaching rate of the cobalt increases quickly when the stirring speed amplified from 700 to 900 rpm. Dissolution ratios of Co, Fe, and Ni in relation to the increasing stirring speed are given in Fig. 8. The highest extraction appeared to be at 900 rpm.
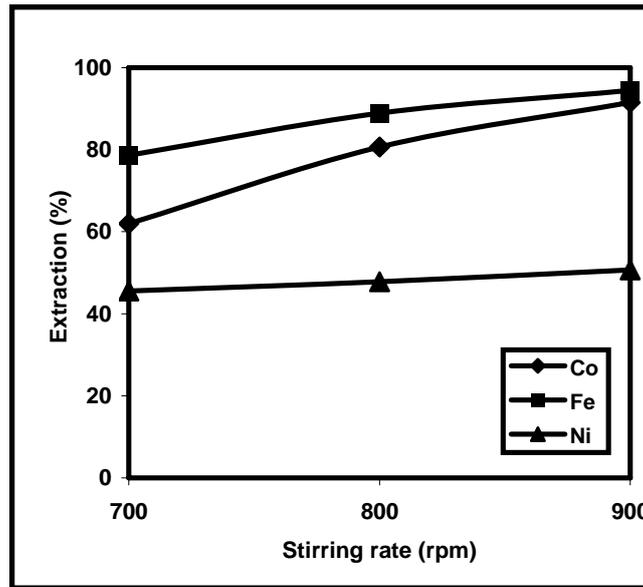
Figure 8: The effect of stirring speed on the dissolution of cobalt and associated elements [-90μm, 25°C, 2h, 0.5 M HNO$_3$, and S/L: 1/10].

It is known that higher stirring rates often result in an increased dissolution rate. In diffusion-controlled processes, the rate of dissolution can be expressed as a function of stirring speed. In this case, the process is diffusion controlled and the boundary layer thickness decreases with increased speed of stirring.

3.1.5. Effect of particle size

The effect of particle size was studied using two ground size fractions of -90 μm and -250+90 μm at 25°C, 2 h, 0.5 M HNO$_3$, 900 rpm, and 1/10 solid/liquid ratio. It is found that smaller particle sizes result in a more efficient leaching of cobalt.

As seen from Table 3, leaching efficiencies are less than the ones obtained with particle size of –90 μm, which shows the effect of particle size.

Table 3: Effect of particle size on the dissolution of cobalt and associated elements [25°C, 2h, 0.5 M HNO$_3$, 900 rpm and S/L: 1/10].

Particle size	Co %	Fe %	Ni %
-90 μm	91.5	94.5	50.7
-250+90 μm	68.5	49.1	54.1

3.1.6. Effect of solid/liquid ratio

Table 4 and Fig. 9 give the cobalt recovery during leaching, as a function of the S/L ratio. According to experimental results presented in Fig. 9, it was found that the cobalt extraction increases with decreasing S/L ratio at ratios higher than 1:10, there was no significant increase in the cobalt recovery.

Table 4: Effect of solid/liquid ratio on the dissolution of cobalt and associated elements [-90μm, 25°C, 2h, 0.5 M HNO₃, and 900 rpm].

S/L	Co %	Fe %	Ni %
1/10	91.5	94.5	50.7
1/20	44.8	55.1	31.4
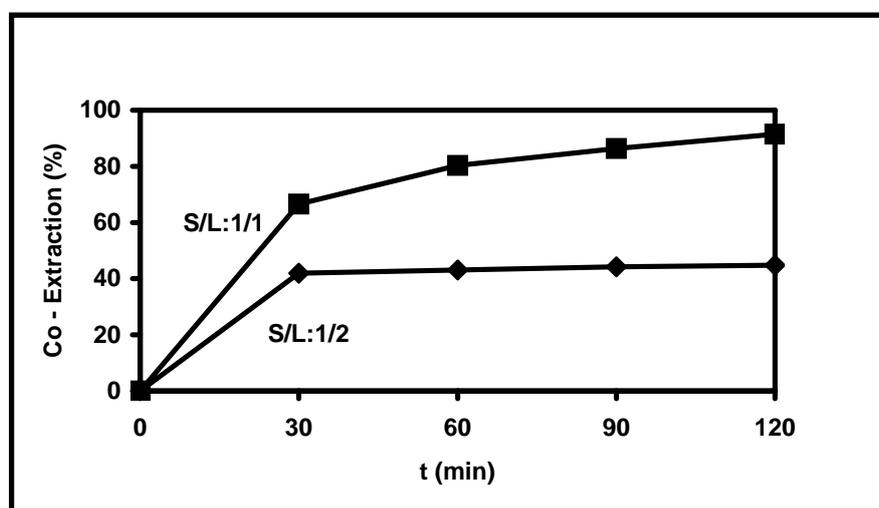
Figure 9: The effect of S/L ratio on the dissolution of cobalt [-90μm, 25°C, 0.5 M HNO₃, and 900 rpm].

3.2 Precipitation of cobalt hydroxide

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. A strong alkaline such as sodium hydroxide is often used as a precipitating agent for metal hydroxides. After addition of sodium ions the leach solution cobalt hydroxide starts to precipitate immediately. The theoretical background of hydroxide precipitation can be explained by the help of a Pourbaix diagram. As Fig. 10 shows Cobalt hydroxide [$Co(OH)_2$] precipitation is possible above pH 5 at 55 °C.
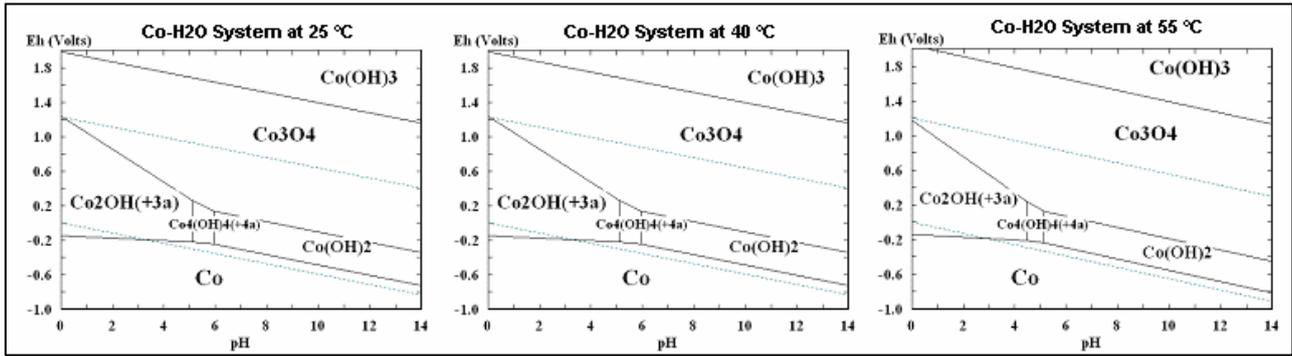
Figure 10: Potential-pH equilibrium diagrams for the system cobalt-water at 25, 40 and 55 °C.

The optimum hydroxide precipitation conditions are obtained at pH=11 and 55°C (see Table 5). The precipitation efficiency of Co is over 98 % at a temperature 55 °C and pH 11 respectively. 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, depending on the precipitation conditions. It is commonly used as a starting material in the synthesis of cobalt chemicals [13].

Table 5: Optimum hydroxide precipitations conditions and impurity analysis of cobalt hydroxide

Initial Solution (mg/l)				Co	Fe	Ni
				4600	10	10
				Precipitation efficiency (%)		
T (°C)	pH	t (min)	NaOH	Co	Fe	Ni
55	11	30	2 M	>98	>98	>98
Chemical composition of cobalt hydroxide (wt%)				55.6	0.04	0.02

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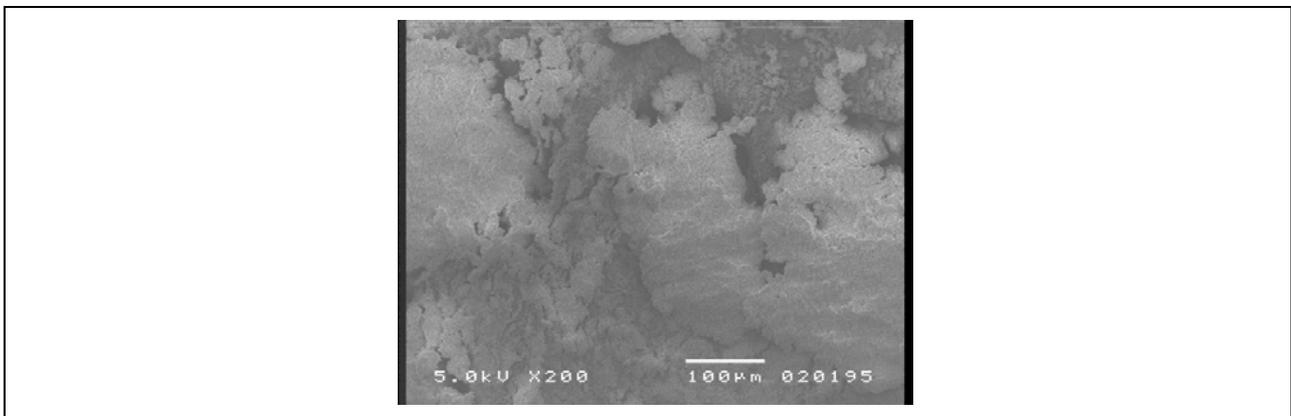
Figure 11: SEM micrograph of the cobalt hydroxide obtained at 55 °C and pH 11

3.3 Waste water treatment

The wash solution of the leach residue and precipitate was combined and reserved for the waste water treatment step. $NaNO_3$ was crystallized via evaporation from the solutions after Co precipitation. The chemical analysis of the $NaNO_3$ is given in Table 6.

Table 6: The chemical analysis of the $NaNO_3$

$NaNO_3$	(ppm)		
	Co	Fe	Ni
	10	5	2

The $NaNO_3$ produced is suitable for chemical and glass industry applications in terms of chemical composition.

3.4 Thermal decomposition 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 decomposition 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 decomposition 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. 12) 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** |
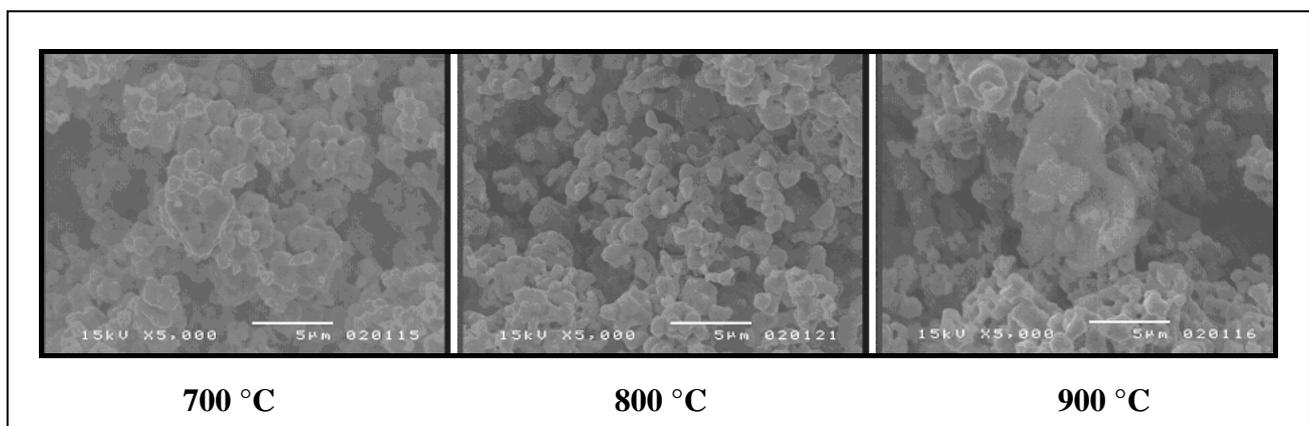
Figure 12: SEM micrographs of the cobalt powder

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 7.

Table 7: 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 8.

Table 8: Typical proporties 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

Recycling of cemented carbide scrap is becoming increasingly attractive. In this investigation, a three-stage process flow sheet has been developed for Co recovery from the cemented carbide scraps. This technique represents an alternative to the classical recycling techniques. The optimum leaching conditions are determined to be as -90 μm, 25°C, 2 hours of leaching period, 0.5 M HNO3, 900 min−1, and S/L ratio of 1/10. Cobalt can be more efficiently dissolved when the fraction of −90 microns particle size was used. Particle size of the cemented carbide scrap can easily be decreased below 90 microns through classical grinding processes. The highest leaching efficiency was attained at 25°C and temperature does not seem to affect the leaching efficiency of cobalt. Stirring speed, however, has a determining role on the leaching. 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 m^2/g.

Acknowledgments

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