

# A new sustainable approach in recovering Cobalt from “hard metal” production by-products

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## Abstract

The present work shows the capability of Maleic Acid solutions to tune the amount of Co in cemented carbide-based recovery powders with a Co content exceeding the threshold (10% Co) for industrial manufacturing in Hard Metal production and required by safety regulations. Maleic acid solutions react promptly and selectively in very mild conditions (0.5M, room temperature and pressure, EtOH as solvent) with Co contained in WC-Co sintered powders obtaining the  $[\text{Co}(\text{Mal})_2(\text{H}_2\text{O})_4]$  compound almost quantitatively. Characterization of the resultant recovery powders (SEM-EDS, XRD) and reaction solutions (ICP-OES) after treatments confirmed the almost complete Co removal and high leaching efficiency. Recovery powders deprived of Co demonstrated proper quality to be re-employed in the production process. These results seem really promising in providing a novel, tunable and effective remediation of this hazardous industrial waste and preserve raw material depletion.

**Keywords:** Hard Metal, Critical Metals, Recycling, Cobalt, Maleic Acid

## 1. Introduction

Cemented carbides (primarily WC-Co) also known as “Hard Metals” (HM) are a class of sintered composite materials widely utilized for over a century in the fabrication of mechanical, cutting, mining and related tools, on account of their ability of imparting them excellent wear resistance, mechanical strength, hardness and toughness (Ortner et al., 2015; Edtmaier et al., 2005; Lee et al., 2011; Shibata et al., 2014). Current industrial production of WC-Co materials leads to the formation of unwanted byproducts, mainly in the shaping tools manufacturing phase, which are rich in cobalt and require treatment in order to lower Co content below the practical and legal working limit (10 wt%). Given the high cost and difficulty of treating these powders, it would be beneficial from both environmental and economic perspectives to develop methods for properly tuning the Co content (Edtmaier et al., 2005; Shibata et al., 2014; Kanerva et al., 2016), as well as fully recovering Co and W from HM scraps implementing a circular economy model. Currently, a variety of methods including chemical modification (Lee et al., 2011), melting metallurgy and “zinc

process” (Freemantle and Sacks, 2015), cold stream and operations using strong inorganic acids (phosphoric, sulfuric, nitric or hydrochloric acids) (Kojima et al., 2005; Yang et al., 2016; Yang et al., 2017; Kim et al., 2014) have all been proposed and are unfavorable due to the very harsh conditions they require (being mostly unselective, they use reactants and/or conditions able to completely react with WC besides Co), and the formation of tungstic acid which is deposited in the pores of the leached zones (Malyshev and Gab, 2007). Thus, the design of a more sustainable method, based on the use of safe reactants able to dissolve the Co binder selectively leaving WC unchanged and ready to be reused in the process would represent an important improvement for industrial and environmental perspectives. In this paper, the use of diluted ethanolic solutions of Maleic Acid (**H<sub>2</sub>Mal**,  $\text{HO}_2\text{CCH}=\text{CHCO}_2\text{H}$ , *cis*-Butenedioic acid,) is described.

## 2. Materials and Experimental Methods

Co powder and WC-Co recovery powders (RC-627C and RC-631L), byproducts of HM production, were provided by F.I.L.M.S. S.p.A. - OMCD Group. The Co content of the binder phase in the latter samples was 19.55 wt.% and 20.4 wt.%, respectively. All chemicals were of reagent grade and used as purchased by Sigma Aldrich.

Co-leaching experiments on recovery powders were effected reacting the sample (500mg) with an ethanolic solution of H<sub>2</sub>Mal (250mL, 0.5M) at room temperature under magnetic bar stirring and monitoring the process in the 1-24hrs by 1h steps. At the end of each reaction, the solution was separated from the powder via filtration. A measured amount of the leaching solution underwent microwave digestion and following ICP-OES analysis in order to quantify the amount of leached cobalt. Solid  $[\text{Co}(\text{Mal})_2(\text{H}_2\text{O})_4]$  was easily precipitated from the leachate by adding acetone to the solution and fully characterized. Solide residue of WC after leaching, was characterized by p-XRD and SEM-EDS (not reported).

## 3. Results and Discussion

Maleic Acid was selected as a selective leaching agent for cobalt due to its low pKa (1.83) among the “weak” organic acid family, its relatively low cost and its good

solubility in ethanol. The use of alcohols as solvents in site of water on treating HM powders, is really desirable because, besides some critical aspects such as cost and flammability, they are able to limit undesired oxidation phenomena on the WC surface, as well as they can easily be recycled at the end of the process avoiding wastewaters.

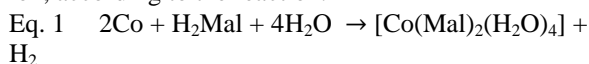
### 3.1 Leaching experiments on Co powder

20mg of Co powders were reacted with 50mL of H<sub>2</sub>Mal ethanol leaching solution at concentration ranging from 0.1 to 1M at room temperature under stirring. Leaching times are summarized in Table 1.

**Table 1.** Co powder-leaching times by H<sub>2</sub>Mal (EtOH) at room temperature under magnetic bar stirring. Results obtained as average value of two repetitions.

Lixiviant Concentration (M)	Leaching Time (h)
0.1	3
0.5	3
1	2

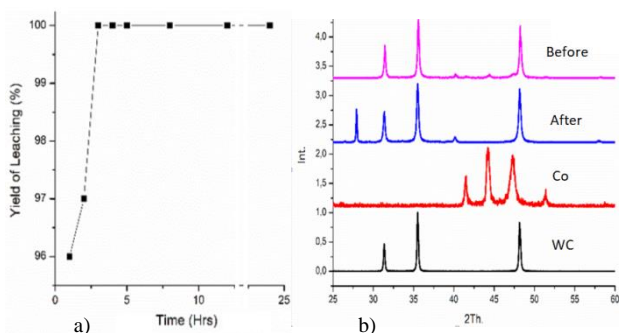
As shown, H<sub>2</sub>Mal solutions demonstrated high efficiency still at low concentration level, dissolving almost quantitatively Co-powder in short time. The leaching reaction occurs by oxidation and simultaneous complexation of the metal forming, in a single-stage, the complex [Co(Mal)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>], where Mal=maleate ion, according to the reaction:



The solution turns from colorless to bright pink with the formation of the Co(II) compound and metallic Co disappearing. These satisfactory preliminary results stimulated further studies on real samples.

### 3.2 Leaching experiments on recovery powders

Figure 1 shows the leaching profile, in terms of yield % vs t, obtained by monitoring on the leachate the amount of leached Co in the time from 500mg of the RC-627C recovery powder, by means of a 0.5M H<sub>2</sub>Mal solution in EtOH at room temperature.



**Figure 1.** a) Co-leaching yields from 0.5g RC-627C (19.55%Co): H<sub>2</sub>Mal 0.5M, EtOH 250mL, r. T., stirring, observation time 24h; b) p-XRD on RC-627C before and after leaching.

As shown, still after 3 hrs Co was completely removed from the sample, reaching an almost quantitative yields in the two previous hrs as well. A larger scale experiment, was hence performed on 300g of RC-631L in order to provide the company a treated sample in amount compatible with testing the material. Under the above reported conditions, around the 75% of Co was removed leaving a 5% Co into the solid residue. This result is a good agreement with the characterization made by the company on this residue, who confirmed the good quality of the material after leaching.

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