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# A new facile *solvo*metallurgical leaching method for the selective Co dissolution & recovery from *hard metals* waste.

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KEYWORDS. Carbides • Cobalt • Green Chemistry • Maleic Acid • Waste Prevention.

## ABSTRACT

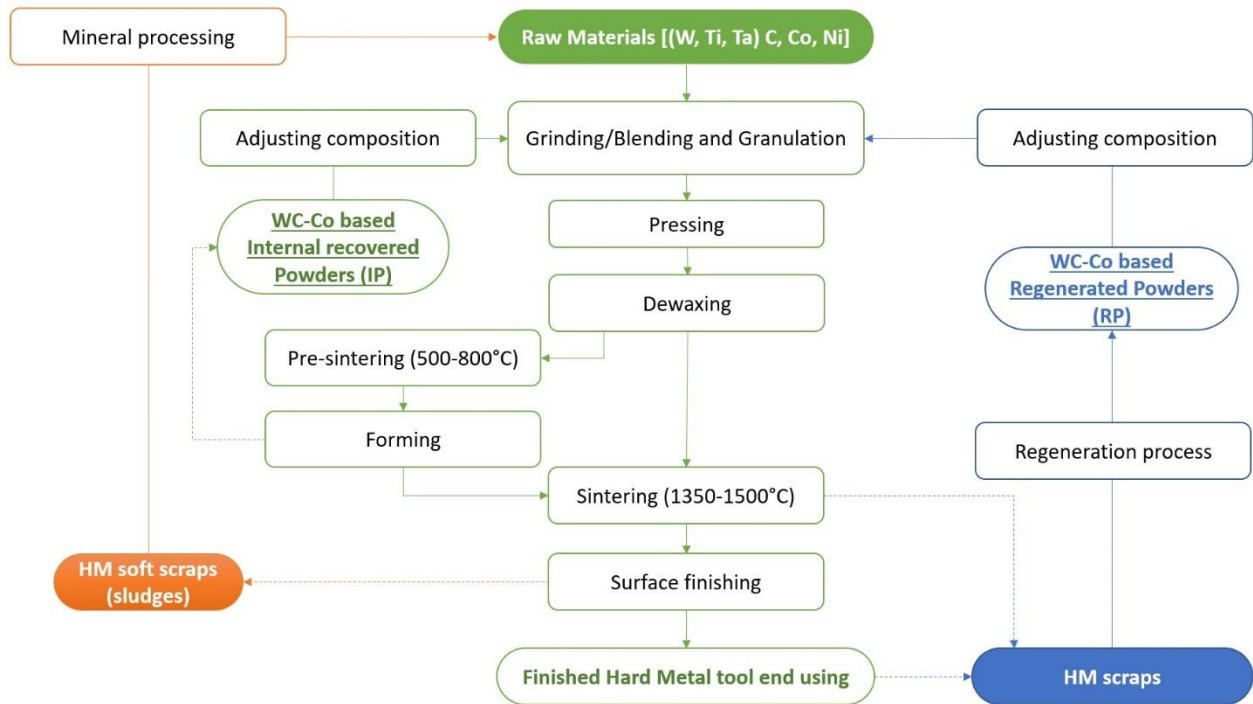
Hard Metals (HM) production plays a fundamental role in economy and technological development. Due to the criticality of its main raw materials, W and Co, a sustainable HM waste recycling is hence desirable for both environmental and economic reasons and strongly encouraged by European waste management directives. This work describes a new *solvo*metallurgical leaching method based on diluted maleic acid (H<sub>2</sub>Mal) ethanolic solutions, which demonstrated to couple effectiveness in materials enhancement from HM waste, with mildness and sustainability of operative conditions. Specifically, H<sub>2</sub>Mal (0.5 M, EtOH) selectively and quantitatively leached Co trapped within WC-Co powders, to afford [Co(HMal)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>] complex within 4 h at room temperature and leaving WC unreacted and ready for re-employment in HM manufacturing. Characterization of the resultant materials i.e. treated powders (SEM-EDS, p-XRD, ICP-OES) and Co-leaching solutions (ICP-OES), confirmed the near quantitative Co removal as well as the possibility to finely tune the composition of WC-Co mixtures. Parameters for best leaching conditions, i.e. time and liquid-to-solid ratio, were obtained. A scale-up experiment addressed to test the leaching conditions and the quality of the recycled material is also described. The quality of the recycled material for direct re-employment in HM manufacturing was validated by Metallurgical Quality Control, to good effect. Finally, preliminary experiments on cobalt metal

recovery from the metal complex by electrowinning and by quantitative precipitation as  $\text{CoCO}_3$  were performed with encouraging results: a step forward resources circularity.

## 1. INTRODUCTION

Cemented carbides, also named Hard Metals (HM), are widely used in the fabrication of mechanical, cutting, mining and related tools, on account to their ability to impart them excellent wear resistance, mechanical strength, hardness and toughness.<sup>1</sup> HM are typically obtained through powder metallurgy and are constituted of refractory transition metal carbides - mainly WC but also Ta-, Mo-, Nb-, Ti-, V- and Cr- carbides - embedded within a metallic matrix working as a binder.<sup>2</sup> Depending on the specific application of HM, the use of cobalt, nickel and iron-based alloys as matrix constituents, has attracted considerable attention, with Co being the most popular binder metal.<sup>1</sup> It is worthy to note, the peculiar properties of HM strictly depend on the composition/granulometry combination of the WC and Co mixture, hence needing a careful control in order the final hard material to be functional for application. Despite ligand metal loading may span between 3 and 30% of Co and granulometry from 0.2 (ultrafine) to  $>6\ \mu\text{m}$  (extra-coarse), the composition that is most largely diffused on the market contains 7-9% of Co with a 0.7-1  $\mu\text{m}$  (submicron-fine) granulometry. Thus, W and Co represent the main raw materials for industrial HM manufacturing with a demand by application in 2017 of 67200 and 8120 t, respectively, representing the 64% and 8% of the worldwide demand for these metals.<sup>3</sup> Since 2010, W and Co are listed among the critical elements by the EU due to their high and growing economic importance and the risks related to their supply.<sup>4,5</sup> Furthermore, in 2011 the European program for Registration, Evaluation, Authorization, and Restriction of Chemical substances (REACH)<sup>6</sup> and the U.S. National Toxicology Program (NTP)<sup>7</sup> classified cobalt powder with particle size  $<4\ \mu\text{m}$  as an inhalable, toxic and carcinogenic material. On account of the environmental and economic

aspects, both governments and manufacturers propel actions for increasing the recovery and recycling rate of W and Co from industrial HM by-products and scraps. Typical by-products of the current industrial production of WC-Co materials are the powders obtained and collected in shaping the tools after the pre-sintering phase of the manufacturing process (Figure 1). These powders, namely Internal Powders (IP), show fixed WC-Co composition and granulometry, against the tunability required for direct re-employment in HM manufacturing. In some cases, IP may contain very high Co amount ( $>10$  wt. %),<sup>6,8</sup> making them problematic toxic wastes difficult to be re-employed for HM production and managed.



**Figure 1.** Simplified metallurgical process for HM tools production and internal powders recovery (green line), external waste regeneration (blue line) and recovery (orange line), which highlights WC-Co based recovered material (Internal Powders, IP, and Regenerated Powders, RP) of interest for this work.

Similarly, regeneration processes for HM end-of-life tools enhancement, namely *direct recycling*, may produce semi-finished WC-Co powders (Regenerated Powders, RP), that need a fine tuning of the Co content for making them reusable for practical purposes.<sup>9,10</sup> Besides those so called “hard” scraps, “soft” scraps consisting in sludges of sintered carbide fragments and silica in a water/oil media, are also produced in the harsh surface finishing phase of the HM manufacturing process. In this context, developing sustainable methods for recovering W and Co from these wastes would be beneficial from both environmental and economic perspectives, impelling resource circularity.<sup>4</sup>

The most versatile and powerful recycling approach currently in use for industrial HM wastes enhancement is the *chemical modification* (also called *indirect recycling*) typically applied for mineral processing and to a wide range of W-based materials. Indeed, it is able to intimately transforming the material structure and composition by a series of combined high temperature oxidations and chemical (alkaline and/or acidic)/electrochemical treatments, achieving high-purity raw materials suitable for a great deal of applicative purposes.<sup>9,11,12</sup> Against, they often involve energy- and chemicals-intensive treatments which require expensive equipment, complex plants and skilled workers. In this context, binary- and ternary-phase tungsten materials, e.g. WC-Co-based powders and scraps, can be alternatively approached by a more selective acidic leaching able to dissolve just one phase, primarily the binder, leaving WC phase almost unreacted (*semi-direct recycling*). Strong inorganic acids (phosphoric, sulfuric, nitric, hydrochloric acids) are typically used for this purpose.<sup>13</sup> Besides their high effectiveness in Co dissolution, the use of strong and oxidizing acids like phosphoric, sulfuric and nitric often leads to W transformation to tungstic acid, which is deposited in the pores of the leached zones, hampering cobalt leaching and requiring further treatments for recycling. Furthermore, these processes heavily threatens the

environment and operators due to the harmfulness of reagents and gaseous by-products.<sup>11,14</sup> On the other hand, chloric acid demonstrated to prevent oxidation phenomena but still rises safety concerns due to the high concentration (6M) of hot (110°C) acidic solutions.<sup>15</sup> An appealing alternative is the use of safer and easily available organic acids which can work as selective leaching agents for Co. A promising attempt of direct hydrometallurgical leaching of Co from WC-Co HM scraps was proposed using acetic acid (concentration: 3.6 M; pressure: 1–5 kPa; T: 40-80°C; t: 2.6-6.5 days) in the presence of oxygen achieving a quite satisfactory 85% Co-leaching yield, leaving WC almost unreacted and ready for re-employment for HM production.<sup>16</sup> This fundamental finding demonstrates, as also found in the satisfactory treatment of oxidized WC-Co materials ( $\text{WO}_3/\text{CoWO}_4$  composition)<sup>17</sup> and other different Co-containing scraps,<sup>18</sup> the potentiality of using eco-friendly weak organic acids as a valued alternative to the hazardous less selective strong inorganic acids more widely used in this field. Nevertheless, the effectiveness of this approach is in some way limited by the relatively high  $\text{pK}_a$  of the acetic acid which, indeed, require the addition of an external oxidant, i.e.  $\text{O}_2$  under pressure, for promoting the leaching. Despite the easy availability of gaseous  $\text{O}_2$ , its low solubility in water heavily affects the reaction rate. In order to overcome this limitation, organic acids, such as acetic or formic acids, were proposed acting on WC-Co materials in the presence of a stronger and water soluble oxidant,  $\text{H}_2\text{O}_2$ , with promising results.<sup>13</sup> However, undesired oxidation/hydration phenomena on the recovered WC particles' surface, mainly due to the use of water as solvent<sup>19</sup> and of strongly oxidizing  $\text{H}_2\text{O}_2$  which interacts with both W and WC,<sup>20</sup> are observed.<sup>21</sup> WC-Co powders with  $\text{O}\% > 0.40$  would result in poor quality HM tools which hence require thermal treatments under reducing conditions for achieving the desired powder composition for HM manufacturing. In that sense, the use of organic solvents for leaching sounds as an intriguing alternative to water systems. As previously defined by

Binnemans & Jones,<sup>22</sup> the term "*solvometallurgy*" refers to metal leaching and extraction when non-aqueous solutions are used, where non-aqueous does not necessarily mean anhydrous, but a solvent with a low water content. Several cases of *solvometallurgical* leaching were proposed as a powerful but sustainable tool for critical metals recovery (and inertization) from Hi-Tech waste,<sup>23</sup> even more when water leaching may interfere with materials and/or recycling processes. In the present case, the working hypothesis is that the use of sustainable organic solvents like alcohols for leaching HM powders would be particularly desirable because it promises to prevent undesired oxidation and hydration phenomena on the WC surface large amounts of water may impel. Among alcohols, ethanol seems particularly appealing being renewable, increasingly available, easy to transport, safe to handle, biodegradable, low in toxicity and largely produced from biomasses, plants and wasted materials.<sup>24</sup> Nevertheless, a limited number of organic acids show an appreciable solubility in ethanol. Among them, H<sub>2</sub>Mal is characterized by a quite low pK<sub>a1</sub> (1.83) and a well-known complexing behavior towards Co.<sup>25</sup> Moreover, it is a relatively low cost acid, which can be produced easily by fungi, such as *Aspergillus Niger*, from renewable substrates or synthesized through sustainable biomass-based feedstocks catalytic conversion or combined photochemistry and bio/electro-chemistry.<sup>26</sup>

On these bases, the Co-leaching properties of ethanol solutions of maleic acid (H<sub>2</sub>Mal) will be here described. The best leaching conditions will be then pointed out and applied on WC-(20%)Co powders, with the goal of appropriately tuning their Co-composition (<10% Co) and fully valorize the recovered materials for industrial purposes. Preliminary results on valued cobalt metal recovery from the leaching product, will be also discussed. Finally, an attempt of sustainability assessment on this process in comparison with the main *semi-direct* hydrometallurgical treatments of WC-Co-based materials, will be proposed on the basis of *green chemistry* principles.<sup>27</sup>



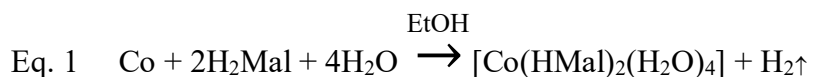
## 2. RESULTS AND DISCUSSION

### 2.1. Leaching experiments on Co powder

Preliminary experiments addressed to study the chemical reactivity of the selected lixiviant towards cobalt metal were performed by reacting Co powders with a calculated excess of H<sub>2</sub>Mal solutions in ethanol (96%) at a concentration of 0.1, 0.5 and 1 M at room temperature under magnetic bar stirring (see details in 4.2.1. section). H<sub>2</sub>Mal solutions demonstrated a remarkable efficiency still at low concentration level, dissolving almost quantitatively Co-powder within 4 h by leaching with 0.1 and 0.5M H<sub>2</sub>Mal solutions, and 3 h with H<sub>2</sub>Mal 1M. As a comparison, much less efficiency was found in preliminary experiments with citric (H<sub>3</sub>Cit) and lactic (HLac) acid solutions in the same experimental conditions (see ESI, S2 section, for details), where complete Co dissolution was achieved in around 12 and 38 h, respectively, at 1M concentration. This finding agrees with the increasing weakness of the acids in the order H<sub>2</sub>Mal < H<sub>3</sub>Cit < HLac (pK<sub>a1</sub> in water = 1.83, 3.13 and 3.86, respectively), even more significant in ethanol with respect to water, and with the decreasing evidence of H<sub>2</sub> gas evolution during the reaction along the series (inappreciable for HLac).

Due to its high efficiency still at very mild conditions with no need of external oxidants and giving a reaction where no precipitations occur, H<sub>2</sub>Mal confirmed to be the most promising candidate for the selective Co-leaching application proposed in this study.

The leaching reaction behind the selected process occurs by oxidation and simultaneous complexation of the metal forming, in a single-stage, the known complexes [Co(HMal)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>] where HMal<sup>-</sup> = hydrogen maleate ion, according to equation 1:



as demonstrated by the extensive characterization of the solid compound (see ESI, S3 section, for CHN elemental analysis, FT-IR, STA, single-crystal X-Ray), crystallized by the leachate through solvent evaporation and acetone washing, as well as by the gas development observation. In the formed compound two  $\text{HMal}^-$  units coordinate the metal center as monodentate ligands and four water molecules complete the coordination sphere. Despite the low water content in the solvent (96% ethanol, 4%  $\text{H}_2\text{O}$ ), water seems playing a relevant role in the coordination. For this reason, the effect of the amount of water contained in the solvent was assessed by repeating the same experiment at  $[\text{H}_2\text{Mal}] = 0.5\text{M}$ , in EtOH 99.99% and in a EtOH/ $\text{H}_2\text{O}$  mixture 90:10. As expected, the reaction run in EtOH 99.99% needed over 8h for dissolving cobalt completely while, similarly to what observed in EtOH 96%, the one run in the EtOH 90% needed just 4h. The experimental evidence, hence, supports the role played by water in the reaction, nevertheless demonstrates that EtOH 96% provides enough water for making complexation occurring efficiently, without requiring undesired large amount of water.

Finally, in order to point out possible by-reactions (e.g. esterification reactions between  $\text{H}_2\text{Mal}$  and EtOH), a further experiment in strictly stoichiometric conditions, was attempted. Specifically, Co powder and  $\text{H}_2\text{Mal}$  were reacted in a 1:2 molar ratio (375mg of Co with 50 mL  $\text{H}_2\text{Mal}$  0.5M in EtOH 96% at r.T). Under these conditions, the leaching reaction occurred quantitatively, leaving no metallic cobalt unreacted. This result demonstrates that, among the competitive reactions involved in solution, the cobalt leaching, driven by the coordination equilibrium, prevails, and by-reactions may be considered negligible.

The satisfactory preliminary results obtained on Co-powder stimulated further studies in order to improve the experimental conditions and to apply the designed  $\text{H}_2\text{Mal}$  *solvom*etallurgy leaching method on real samples.

## 2.2. Leaching experiments on WC-Co test specimens

**2.2.1 Test specimen selection and characterization.** Two samples of WC-Co IP, RC-627C and RC-631L, were considered in this study. The test specimens were fully characterized as detailed in ESI, S1.1. and S1.2. sections, in terms of chemical composition and morphology, respectively. Table 1 summarizes the results obtained by ICP-OES chemical analysis on the digested materials and C and O elemental analysis on solid samples. As shown, the composition of the two powders is very similar, with an approximate 20% of Co binder into the mixture.

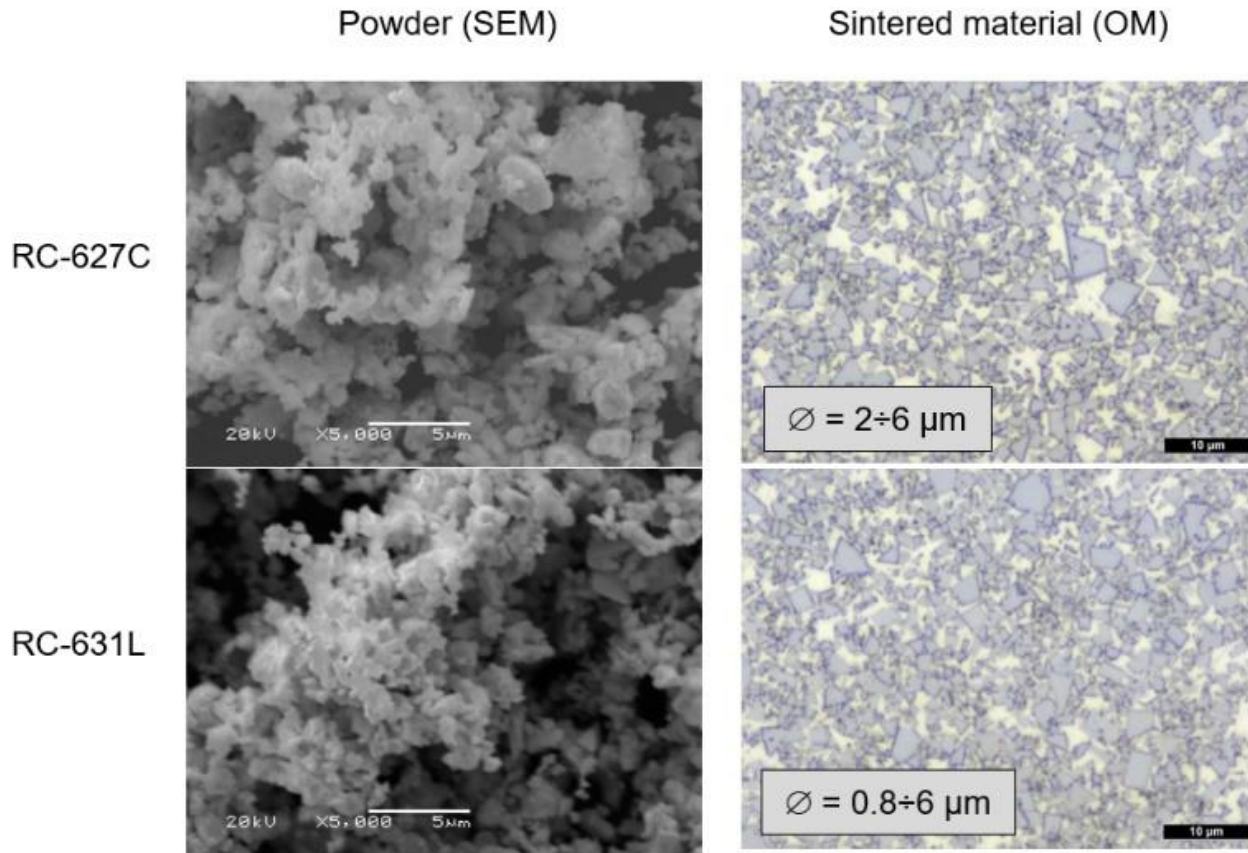
**Table 1.** Metal composition (wt. %) of the recovery powders (RC-631L and RC-627C) used throughout the present study.

Sample	Elemental analysis (wt. %)				
	W <sup>a</sup>	Co <sup>b</sup>	Trace elements <sup>c</sup>	C <sup>d</sup>	O <sup>d</sup>
RC- 631L	72.74	20.40	1.34	4.94	0.58
RC-627C	73.88	19.55	1.05	4.93	0.59

<sup>a</sup>Calculated by difference. <sup>b</sup>ICP-OES analysis on digested materials. <sup>c</sup>Fe, Ni, Ta, Ti, Nb. <sup>d</sup>C and O elemental analysis.

In terms of morphology, the WC grain size distribution was evaluated by image analysis methods. Figure 2 shows SEM and optical micrographs of the two test specimens and the corresponding sintered samples, respectively.

**Figure 2.** Scanning Electron Microscopy (SEM) and Optical Microscopy (OM) micrographs of



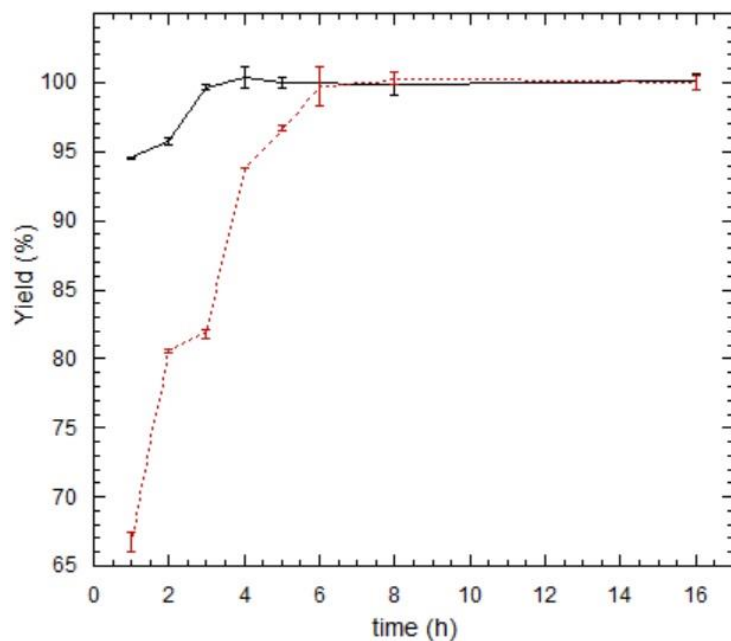
RC-627C and RC-631L test specimens and related sintered materials, respectively.

Test specimens differ mainly for the WC grain size and the mean free path value. Specifically, RC-631L shows a wider grain size distribution than RC-627C that is more conveniently appreciated by studying the grain size distribution they impart to the corresponding sintered materials (evaluated according to ISO 4499-2:2008). Indeed, RC-627C determines a grain size in the  $2\div6\ \mu\text{m}$  range, while RC-631L a grain size in the  $0.8\div6\ \mu\text{m}$  range, in the corresponding sintered HM products which result in different properties and classification of these materials. According to Exner and Gurland,<sup>28</sup> the mean free path is a measure of the thickness of the cobalt layers on WC grains and depends on both the cobalt content and the particle size of the material. Thus, with a similar metallic binder volume fraction, the microstructure of the RC-627C powder mixture will

show a higher mean free path value than RC-631L.<sup>29</sup> Mean free path value may affect the reactivity of the binder phase. Indeed, W-Co solid solution layers form during thermal processing at the interface between WC grains and Co phase. It was experimentally observed they are capable to ennobling (i.e. increasing the reduction potential) the adjacent Co-phase making it less prone to be oxidized.<sup>30</sup> Thus, the higher the contact surface between W-rich layer and binder phase, the lower the expected Co-reactivity. The choice of the two powder samples aimed to highlight the effect of the mean free path value on the leaching process.

**2.2.2. Small scale leaching tests.** Figure 3 shows the Co-leaching profiles, in terms of yield of leached cobalt (wt. %) *vs* time (h), obtained by monitoring the amount of cobalt in the leachate of the RC-627C and RC-631L samples in time (1 h steps) at the most balanced conditions applied to Co-powders (H<sub>2</sub>Mal 0.5M, r.T.).

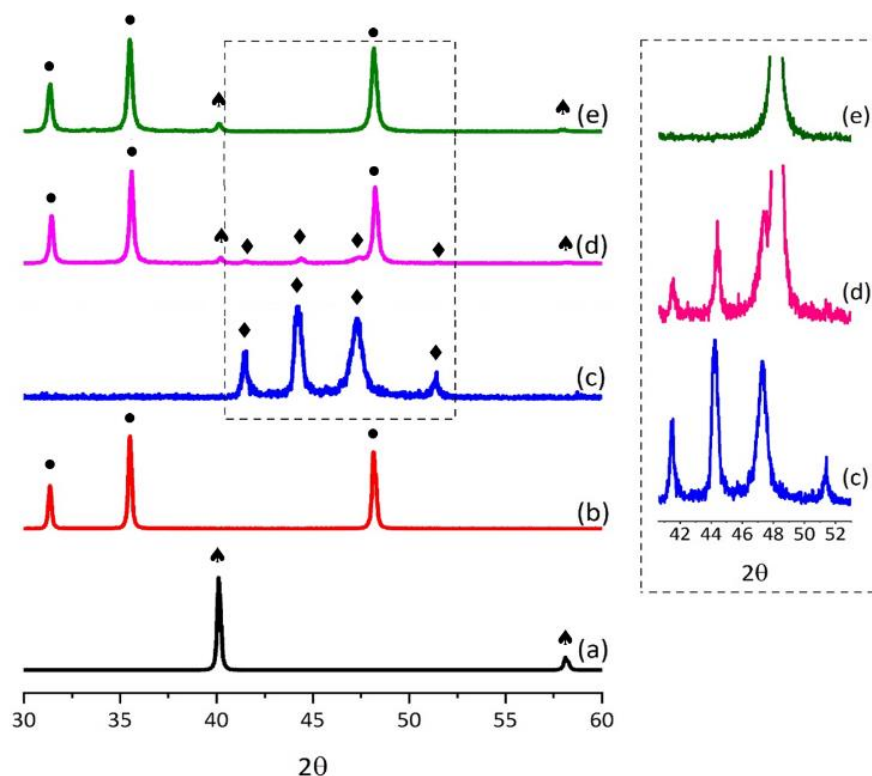
The Co amount in the leachate was determined by ICP-OES on measured aliquots of the solution. As shown in Figure 3, both test specimens reacted promptly to the leaching, obtaining very high yields of Co removal in a short time. Specifically, the leaching system performed better with the RC-627C powder obtaining a very satisfying 96% yield after just 1 h and complete Co removal within 3 h. As expected, slightly lower effectiveness was found with the RC-631L sample, which allowed a satisfactory 94% yield after 4 h and a complete Co removal in 6 h. This slightly different behavior can be reasonably attributed to the lower values of the metallic binder mean free path in the RC-631L sample.<sup>31</sup>



**Figure 3.** Co-leaching profiles from RC-627C (black line) and RC-631L (red line) WC-Co powders on varying the leaching times (1-16 h). Experimental conditions: 0.5 g of RC-627C and RC-631L; 0.5 M  $\text{H}_2\text{Mal}$  EtOH solution (250 mL); room temperature and pressure; stirring (300 rpm). Results are reported as the average value of three independent repetitions.

These results were supported by solid-state characterization of the powders deprived by Co. Figure 4 compares the p-XRD patterns for the RC-627C sample before and after a 4 h leaching, with the patterns for Co metal e WC as references.

**Figure 4.** P-XRD patterns of: a) W powder (♣, JCPDS card 04-0806); b) WC powder (●, JCPDS



cards 65-8828 and 51-0939); c) Co powder (◆, JCPDS card 5-0727); d) RC-627C before Co-leaching; e) RC-627C after 4 h leaching. In the zoom, magnification of c), d and e). Patterns collected for the RC-631L samples, before and after leaching, were superimposable to those of RC-627C samples and are omitted.

The XRD patterns plotted for RC-627C and RC-631L samples before and after leaching, clearly showed the disappearance of Co metal peaks after treatment, highlighting the dissolution of cobalt in the H<sub>2</sub>Mal solution after 4 h leaching. Furthermore, the patterns collected after treatment showed no changes in the other parts of the spectrum, demonstrating the capability of ethanolic maleic acid solutions to dissolve Co selectively leaving W and WC unreacted. SEM/EDS measurements on RC-631L confirmed p-XRD results (see ESI, S4 section), being able to point out the expected small residual amount of Co in this sample (found <1%) after 4 h leaching, in agreement with ICP-

OES characterization of the leachate which suggested a calculated residual 1.2% Co in the powder after treatment.

**2.2.3. Liquid/solid (L/S) ratio optimization.** With the view of meeting industrial requirements for technological transfer and improving the sustainability of the process, experiments addressed to limit the amount of leaching agent and solvent, were performed. Specifically, attempts to fix the Co/H<sub>2</sub>Mal molar ratio to lower values than the previous 1:74 but providing the cobalt a calculated excess of lixiviant and the acid concentration to a still low 1 M, were performed. The experiments were firstly carried out on 0.375 g of Co-powder at room temperature under magnetic bar stirring, monitoring the time of complete disappearance of Co powder from the reaction vessel. Table 2 summarizes Co-leaching times and experimental conditions applied on Co-powder.

**Table 2.** Approximated Co-powder leaching times by varying the Co/H<sub>2</sub>Mal molar ratio.

Co/H <sub>2</sub> Mal	Volume (mL)	L/S*	Leaching time (h)
1 : 4	25	14	6
1 : 8	50	28	5
1 : 12	75	42	5

Experimental conditions: Co powder amount = 0.375g; [H<sub>2</sub>Mal] = 1M; r.T.; magnetic bar stirring 300rpm. \*Calculated values referring to the corresponding amounts of recovery powders 20 wt. % Co.

As shown, keeping all other conditions fixed, as the excess of reagent increases, the leaching times decrease. Co:Acid 1:8 molar ratio seemed guarantee the minimum excess of reagent that allow the leaching to be almost quantitative in 5h. A further increase to 1:12 does not show a significant time reduction. Nevertheless, 1:4 molar ratio still achieves acceptable leaching times allowing furtherly limiting reagent and solvent employment. In these last conditions, as the Co content of the two samples under investigation around 20 wt. %, the L/S ratio was lowered from



the previous 200 L/kg to a more feasible 14 L/kg. Experiments on both RC-627C and RC-631L samples were then performed by using the same amount of test specimen and experimental conditions of previous experiments but providing the powder with 7 mL of H<sub>2</sub>Mal 1 M ethanol solution for respecting the desired Co/H<sub>2</sub>Mal molar ratio and lixiviant concentration. In these conditions, in the face of a substantially lowered amount of employed reagents, the leaching reactions in H<sub>2</sub>Mal led to a more than satisfactory 89.2(±0.2)% and 82.3(±0.3)% cobalt removal in 4 h for RC-627C and RC-631L respectively. These Co-leaching yields correspond to recovered powders with a calculated composition of about WC-(3%)Co and WC-(4%)Co. These results demonstrated the suitability of the improved, more sustainable, operating conditions for providing WC-Co powders with an appropriate composition (Co content <10%) for HM manufacturing.

**2.2.4. Scale-up of the *solvo*metallurgical leaching process.** A larger scale experiment was performed on 300 g of RC-631L in order to obtain a treated sample in amount compatible with testing the recovered materials. The leaching reaction was performed at room conditions for 6 h into a 5 L mixing reactor in the optimized L/S = 14 L/kg, as detailed in 4.2.3. section. At the end of the reaction, the leaching solution was separated by the solid residue by gravity filtration and the two fractions submitted to chemical characterization. ICP-OES cobalt determination on the leachate pointed out a 78% Co-dissolution occurred, which provided an expected WC-(5.8%)Co residual powder. This finding fully agreed with the ICP-OES cobalt determination on the solid residue after digestion where a 6.1% of residual Co was found. Furtherly, C and O elemental analysis performed on the treated sample pointed out that a slightly higher percentage of C (5.99 vs 5.76%) and O (0.65 vs 0.40%) was present with respect to the optimal values. Nevertheless, this very little excess of C and O into the recovered material which can be reasonably related to a minimum residual amount of organic acid after washing, demonstrates that massive

hydration/oxidation phenomena on the sample are prevented by using the proposed *solvo*metallurgical leaching process. Thus, final compositional result of this experiment is completely in line with the need for tuning the amount of Co, providing good quality WC-based recovered powders with a Co content lower than 10%. Further experiments are in progress in order to provide a robust relationship between the starting test specimen composition and the required leaching time for obtaining the desired final Co-percentage.

### **2.3. Assessing the quality of the secondary materials for direct re-employment in HM manufacturing and sustainability for the process**

**2.3.1. MQC and assessment of the WC-based recovered powder.** In order to process the recovered powders and test their quality in HM manufacturing, the treated RC-631L powder was homogenized by lab-scale ball milling as detailed ESI, S1.4 section, then shaped and sintered in forms of small bars to undergo Metallurgical Quality Control (MQC). The results of the MQC procedure are collected in Table 3, where the values of density, hardness (HV10 and HRA), coercitive force ( $H_c$ ) and magnetic moment saturation ( $\sigma$ ) related to the pristine WC-Co powder (RC-631L) are also reported for comparison.

**Table 3.** Results of the MQC on bars obtained by sintering the recovered RC-631L powder after leaching, compared with the same values related to the use of the pristine powder and reference values for a HM with an around WC-(6%)Co composition.

	Density	Hardness		H <sub>c</sub> <sup>a</sup>	σ <sup>b</sup>	Optical Microscopy	
	g/cm <sup>3</sup>	HV10	HRA	Oe	G cm <sup>3</sup> /g	200x <sup>c</sup>	1500x
RC-631L pristine	13.36	933	85.5	94	139	A02	-
<i>WC-(6%)Co</i> <sup>[d]</sup>	<i>14.90</i>	<i>1600</i>	<i>92.3</i>	<i>250</i>	<i>110</i>	<i>A02</i>	<i>-</i>
<b>RC-631L treated</b>	<b>14.88</b>	<b>1609</b>	<b>92.3</b>	<b>228</b>	<b>92</b>	<b>A04</b>	<b>η-phase</b>

<sup>a</sup>Coercive force. <sup>b</sup>Magnetic moment at saturation. <sup>c</sup>Magnification according to ISO 4499-4.

<sup>d</sup>Expected values for HM of WC-(6%)Co composition.<sup>32</sup>

The MQC of bars obtained by the treated powder satisfactorily shows these artifacts possess the metallurgical features, i.e. density and hardness, found for HM materials obtained from virgin Co e W containing 6% of Co.<sup>32</sup> The slightly lower values found for coercitive force and magnetic moment saturation, as well as the presence of the A04 phase instead of the A02 one, are strictly related to the presence of a small unwanted amount of η-phase (a sub-stoichiometric M<sub>6</sub>C or M<sub>12</sub>C carbide phase; see Figure 5). The formation of this phase during the sintering process was expected due to the previously cited little excess of O into the powder. Indeed, the co-presence of C and O into WC-based powders obtains gaseous CO<sub>2</sub> by heating, leaving the sintered material poor in C with the consequent η-phase occurrence in the final material.<sup>33</sup> Noteworthy, in the case of WC-Co powders with a small excess of O, the occurrence in HM of the undesired η-phase can be easily prevented by means of a calculated small addition of C (as high purity carbon black) to the powder during the blending process before sintering. Thus, it can be definitely stated that recovered powders obtained applying the proposed *solvo*metallurgical leaching method fully meet the requirements for HM manufacturing.



**Figure 6.** Schematic diagram for cobalt, reagent and solvent recovery from the leaching solution. Phase A): recycling of ethanol and unreacted H<sub>2</sub>Mal, isolation of [Co(HMal)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>](s); Phase B): alternatively, electrowinning (B1) or Co-precipitation in a commercially viable form (B2).

The tested procedure involves two main phases: A) recycling of ethanol and unreacted H<sub>2</sub>Mal and Co-complex isolation for phase B treatments; B) Co and coordinated H<sub>2</sub>Mal enhancement by electrowinning (B1) or by selective precipitation (B2).

In phase A), the leaching solution obtained as previously described and containing ethanol, the excess of H<sub>2</sub>Mal and the Co-complex, was evaporated under vacuum and ethanol recovered for next treatments. The solid residue was, then, washed three times with acetone for selectively extracting the soluble H<sub>2</sub>Mal by the solid mixture. H<sub>2</sub>Mal and acetone were easily recycled from the resulting solution by gentle heating. In phase B, [Co(HMal)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>], insoluble in acetone, was easily dissolved in a small amount of water to undergo electrowinning (B1). Preliminary experiments of Co electrowinning were performed in order to evaluate the energy efficiency reachable during the process. 0.5 M [Co(HMal)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>] aqueous solutions were treated into a two-electrode cell with 12 mm graphite rods under galvanostatic conditions (see ESI, S5.1 section, for details). Two current values, 300 mA and 100 mA for 10 and 30 minutes respectively, were investigated (resulting in 51.7 mA/cm<sup>2</sup> and 17.2 mA/cm<sup>2</sup> current density figures at the cathode, respectively). In both cases, a Co-metal deposition to the cathode was observed (ESI, Figures S6 and S7) and about 87% energy efficiency, calculated as the ratio between the theoretical charge to get the amount of metallic Co at the cathode and the total amount of charge transferred through the cell, was found. The loss of efficiency is reasonably attributed to the expected cathodic by-process  $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$  occurring in water, in agreement with the experimental evidence of gas evolution to the cathode during the electrowinning. With the aim to determine quantitatively the

Co-metal deposition, further experiments on a smaller scale were performed on 25mL 0.03 M  $[\text{Co}(\text{HMal})_2(\text{H}_2\text{O})_4]$  aqueous solutions, using copper spiral cathodic and platinized titanium anodic electrodes, under constant current of 36 mA (resulting in a constant DC density of  $12 \text{ mA/cm}^2$  at the cathode) at room temperature. After 1 h, more than 70% of total cobalt was obtained on the surface of the copper cathode with an energy efficiency of 73.5% and 97.3% of theoretical maleic acid was found in the solution (as pointed out by HPLC measurements). A higher Co metal recovery efficiency of 86.7% was obtained after 2 hours of electrochemical treatment, but the energy efficiency felt down to 43.7% and most of maleic acid was degraded.

These results are still at early stage and the optimization of the electrowinning process exceeds the focus of this work, but they demonstrate the capability of the metal complex to work as a valued precursor for Co-metal by electrochemical reduction.

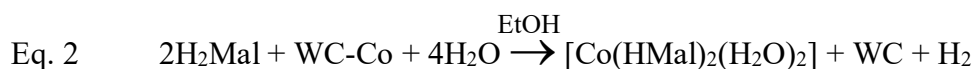
As an alternative, a selective precipitation was tempted adding 12.5mL of  $\text{Na}_2\text{CO}_3(\text{aq})$  0.3M to 25mL of  $[\text{Co}(\text{HMal})_2(\text{H}_2\text{O})_4](\text{aq})$  0.5M. The reaction occurred very quickly, producing an abundant almost quantitative precipitation of  $\text{CoCO}_3$ .  $\text{H}_2\text{Mal}$  was, finally, recovered from the solution after slight acidification by diluted HCl, drying and purification by acetone.

### **2.3.3. Green chemistry metrics and preliminary sustainability assessment of the process.**

With the aim of assessing the sustainability of the proposed *solvo*metallurgical leaching process and following recovery phases, we start from the belief that no industrial process can be considered really *green* if so they are not the chemical reactions it is based on. In that sense, *green chemistry* mass-based metrics can help in pointing out the presence and amount of unsustainable reactants and products as well as the production of waste of a chemical reaction, and they represent a suitable tool for comparing the environmental impact expected for different reactions addressed to obtain

the same products or for similar reactions with the same focus. Table 4 summarizes the metrics calculated for the present work.

Thus, specifically speaking about the proposed leaching reaction:



the first consideration is that this reaction occurs almost quantitatively, in a single stage and selectively, so it can be graded as a high step-economy reaction. Besides, considering  $[\text{Co(HMal)}_2(\text{H}_2\text{O})_2]$  and WC as the desired products, Atom Economy (AE) is calculated to be higher than 99.9%. This value suggests an almost full conversion of the reactants into the valued products. Worthy to note, despite the possible risks related to manage large amount of hydrogen gas, the  $\text{H}_2$  by-product is a valuable energy vector and reactant (e.g. for thermal and chemical reductions) which can be collected and valorized even inside the HM industrial manufacturing plant. Further important information comes from Mass Productivity (MP). This parameter points out the percentage of valorized material in the leaching process. The quite low 14.6% MP value calculated for the proposed process is heavily affected by the non-aqueous solvent – EtOH – whose mass is added at the denominator of the fraction. Noteworthy, EtOH is an environmentally sustainable solvent (listed among the most sustainable solvents) and it is fully recyclable preventing wastewater production.

These very important aspects can be pointed out by calculating the E Factor, which puts in relationship the amounts of desired products with those of generated wastes and represents a good connection between the laboratory and the industrial scale.

**Table 4.** Selection of *green chemistry* metrics applied to the proposed leaching & recovery process.

Metrics	Mathematical expression	Calculated value	Ref.
Atom Economy (AE)	$\frac{\sum \text{m.w. desired products}}{\sum \text{m.w. reagents}} \times 100$	<b>99.9%</b>	[34]
Mass Productivity (MP)	$\frac{\text{Mass desired products}}{\text{Total mass used in the process}} \times 100$	<b>14.6%</b>	[27]
E Factor (EF)	$\frac{\text{Total waste}}{\text{Mass of product}}$	<b>11-7<sup>a</sup></b> <b>9-0.3<sup>b</sup></b>	[35]

<sup>a</sup>Leaching reaction followed by A-B1 recovery process; <sup>b</sup>Leaching reaction followed by A-B2 recovery process.

Despite a strict evaluation of the E Factor is hard to be done and would come from an industrial application of the process, the reported values were estimated on the basis of the lab scale leaching reaction followed by the two tested procedures involving A-B1 or A-B2 recovery phases. E Factor may assume very different values depending on the rate of reagents and solvents recycling at the end of the process. In the case of leaching followed by A-B1 recovery procedures, E Factor may span since 11, when acetone, hydrogen gas and the final H<sub>2</sub>Mal water solution are not enhanced, to 7, when just the final H<sub>2</sub>Mal water solution would be disposed of. Similarly, in the case of leaching followed by A-B2 recovery procedures, E Factor may span since 9, when acetone, hydrogen gas and the final H<sub>2</sub>Mal water solution are not enhanced, to 0.3, when just the residual NaCl would be disposed of. It is noteworthy the highest are the rate of recycling (lowering E Factors), the highest are the recovery costs, mainly in terms of energy. Thus, the best conditions on industrial scale would be the best compromise between rate of materials enhancement and costs for recycling.

This process should be considered in the framework of the *semi-direct recycling* processes. The use of H<sub>2</sub>Mal in EtOH seems more eco-friendly and safe than previously cited strong inorganic



acids in water, thanks to easy-to-handle reagent which produces, besides the desired products, just a very small fraction of valuable by-products (H<sub>2</sub>) and few wastewater. Inorganic acids like HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> are efficient leaching agents for cobalt. Nevertheless, they are not selective leading to a deep transformation of the WC-matrix (formation of H<sub>2</sub>WO<sub>4</sub>) which requires following treatments for obtaining back the desired WC for HM manufacturing. Besides, they are harmful to operators and their action is accompanied by undesired toxic gases evolution (NO<sub>x</sub> and SO<sub>x</sub>, respectively) in large amounts. For these reasons, the step economy and AE of the reactions involved, are expected to be lower than those calculated for the H<sub>2</sub>Mal/EtOH treatment. In that sense HCl is less polluting but still a hazardous leaching agent to be carefully handled by operators. The expected higher MP of these systems is counter-balanced by higher values for the E Factors due to lower rates of reagents recyclability and strongly acidic wastewater production.

Due to the mildness of the leaching action and the low environmental impact of the reagents, acetic acid hydrometallurgy seems closer to H<sub>2</sub>Mal *solvo*metallurgy in terms of environmental sustainability. In this case, the higher pK<sub>a</sub> (4.7) of acetic acid (HAc) as well as the aqueous media, favor the following leaching reaction:



Theoretically speaking, the metrics for this reaction should be close to those calculated for H<sub>2</sub>Mal *solvo*metallurgy leaching. Specifically, step and atom economy are similar, with AE = 100%, with negligible H<sub>2</sub> production. Nevertheless, the relatively low solubility of O<sub>2</sub> in water beside its low diffusion rate through the solution heavily affects the efficiency of the process requiring working with O<sub>2</sub> insufflation and/or under high pressure. This aspect leads to an expected low MP (even if water is not considered in the calculation) and/or more costly equipment and, even more, the presence of undesired hydration/oxidation phenomena on the WC surface which

require further treatments. Moreover, if not well managed, the reaction may produce large amounts of wastewater (high E Factor value).

Despite the valued assessment of the whole technical-environmental-financial sustainability on industrial scale would come only by a full configuration pilot-scale implementation and related more comprehensive Life Cycle Analysis (that will be the focus of future works), it can be argued that the use of a solid reactant that combines complexing and oxidizing properties makes very easy the storage, management and handling of the lixiviant and the reaction easily tunable and effective.

### 3. CONCLUSIONS

H<sub>2</sub>Mal ethanol solutions demonstrated high efficiency in dissolving almost quantitatively and selectively Co from HM wastes in a short time, at low concentration level, room conditions and without the addition of external oxidizing agents. The leaching process leaves WC unreacted and ready to be re-employed for industrial purposes. These experiments demonstrated also the capability of the proposed method to properly lower the percentage of Co in the treated powders, meeting the compositional requirements of the industrial HM manufacturing process. Beside the possible applications of the complex as it is, [Co(HMal)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>] demonstrated to be a valued precursor for Co metal by electrowinning and for the commercially viable product CoCO<sub>3</sub>. The use of a solid, weak organic acid, able to couple oxidizing and complexing properties even in EtOH and which does not produce toxic fumes when reacting as leaching agent, makes H<sub>2</sub>Mal a very versatile, easy-to-handle and powerful reagent for *sol/vometallurgical* leaching. The absence of large amounts of water and appreciable undesired by-reactions, combined with the selectivity, efficiency, and eco-friendliness of the proposed *sol/vometallurgical* leaching process, allows to achieve in one-stage high quality WC-based powders which do not require further treatments for re-employment, making this process an appealing alternative to more aggressive strong acids as

well as organic acid aqueous solutions requiring external oxidants. The recent finding of more sustainable synthetic ways for maleic acid production (e.g. through biomass-based feedstocks catalytic conversion) furtherly stimulates the use of this acid and makes the method described here a very promising alternative to the conventional methods providing both a sustainable remediation tool for hazardous WC-Co industrial waste and raw materials preservation.

## 4. EXPERIMENTAL SECTION

### 4.1. Materials and chemicals

All chemicals were of reagent grade and used as purchased by Sigma Aldrich (EtOH, 96%; maleic acid, 99%) and Bodanchimica (Mixetan 100, EtOH 99.9%) without any purification. Cobalt powder was used as purchased by Umicore (Extrafine, >99.5 wt. %, 1.3  $\mu\text{m}$ ). WC-Co recovery powders (RC-627C and RC-631L), were provided by F.I.L.M.S. Corp. (OMCD Group, Anzola d'Ossola (VB), Italy).

### 4.2. Leaching experiments

**4.2.1. Leaching of Co-powder.** Co powder (20 mg, 0.34 mmol) was reacted with a  $\text{H}_2\text{Mal}$  ethanol solution (50 mL) at room temperature (20-25°C) and pressure under magnetic bar stirring (300 rpm), monitoring the time of disappearance of Co powder on varying the concentration of the leaching agent (0.1, 0.5 and 1 M). The solution turned from colorless to bright pink as the reaction progressed. The Co(II) complex, a product of the leaching process, was easily precipitated in high yield (81%) from the leachate by concentration in a rotary evaporator, acetone addition to the concentrate (1:1 volume ratio) and dried in an oven at 45°C. The desired product,  $[\text{Co}(\text{HMal})_2(\text{H}_2\text{O})_4]$ , was fully characterized and confirmed with respect to literature.<sup>24</sup> Single-crystal X-ray diffraction measurements on a crystalline sample obtained by slow rate diffusion of acetone fumes into the leaching solution further confirmed the sample composition. The full

characterization of the product is provided in the Electronic Supporting Information (see ESI, section S3.4).

**4.2.2. Leaching on test specimen (WC-Co IP).** 0.500 g test specimen aliquots were reacted in an open flask with an ethanol solution of H<sub>2</sub>Mal (250 mL, 0.5 M or 7 mL, 1 M) at room temperature (20-25°C) and pressure under magnetic bar stirring (300 rpm) and monitoring the process in the 1-24 h range. 0.1 mL clear solution aliquots were sub-sampled from the leachate at 1 h intervals and submitted to acid digestion (ESI, S1.3 section). The remaining solid residue containing WC was washed with ethanol and subsequently dried before being characterized (ESI, S1.1 section).

**4.2.3. Scale-up process.** A 300 g aliquot of RC-631L was reacted with an H<sub>2</sub>Mal ethanol solution (1 M, 4.2 L, L/S = 14 L/kg) at room temperature (20°C) and pressure into a 5 L vessel equipped with a mechanical stirring (400 rpm) driven by a Janke&Kunkel IKA-WERK motovariator, mod. RW20. After 6 h, the reaction was stopped and the resulting mixture separated by gravity filtration and collected for characterization. The leaching solution was treated as reported above for ICP-OES characterization. The recovered powder was washed several times with EtOH, dried and then fully characterized as reported above.

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produced by carbothermal regeneration of "hard metal" scrap" project, 2019]. The authors gratefully acknowledge Prof. Luciano Marchiò, University of Parma, for the always fruitful scientific collaboration and his valued contribution in the single-crystal X-ray characterization of the  $[\text{Co}(\text{HMal})_2(\text{H}_2\text{O})_4]$  complex.

**Keywords:** Carbides • Cobalt • Green Chemistry • Maleic Acid • Waste Prevention

## ASSOCIATED CONTENT

The Supporting Information is available free of charge on .....:

- Methods
- Preliminary Co-leaching experiments with  $\text{H}_3\text{Cit}$  and  $\text{HLac}$
- Solid state characterization of  $[\text{Co}(\text{HMal})_2(\text{H}_2\text{O})_2]$ : CH-elemental analysis; TGA; FT-IR; single-crystal X-Ray diffraction data;
- SEM/EDS characterization of RC-631L sample powder before and after 4 h leaching.
- Electrowinning experiments.

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### Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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