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# Trends and perspectives in the use of organic acids for critical metal recycling from Hard-Metal scraps

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**KEYWORDS.** Circular economy • Cobalt • Tungsten • Leaching agents • Organic Acids • Cemented carbides.

## Abstract

Hard-metal sector, strategic for the industrial economies, is suffering from the reduced availability and price volatility of its main feedstock: critical W and Co. In 2021, a 73.5 kt W and 9.2 kt Co demand for hard-metal production (65% and 5.3% of global demand, respectively), was recorded. Hard-metal scrap recycling is hence desirable for both environmental and economic reasons. A significant recovery of W and Co from manufacturing by-products and scraps is already good practice in the hard-metal industry (42% for W and 22% for Co). However, there is still a lot to do to meet the technical-economic-environmental sustainability in materials and energy enhancement for pursuing a green economy model. Indeed, Chemical Modification and Direct Recycling, which are the most widely employed industrial approaches, typically involve energy and/or harsh chemicals-intensive treatments which require expensive equipment and skilled workers. In the last decade, research efforts have been spent on implementing alternative materials reclamation processes from hard-metal scraps based on the use of bio-based organic acids with the view to increase the rate and quality of the recycled materials exploiting their peculiar metal complexing action as well as to preserve natural resources and prevent the disposal of potentially toxic/polluting substances. Despite the preliminary stage of the research, organic acids were demonstrated to be powerful but gentle agents for the selective leaching of cobalt from WC-Co-based materials as well as promising agents for  $WO_3$  dissolution. Indeed, thanks to their acid and complexing properties, they can stabilize metals in their oxidized form giving soluble products and preventing passivation phenomena. Furthermore, organic acids can be obtained by renewable biomass transformation, limiting the request for high-impact industrial chemicals. Hence they points out key features making them promising for the design of eco-friendly recovery processes. In this context, the different industrial approaches to the recovery and recycling of Hard-metal wastes, with specific reference to the role of bio-derived organic acids in hydro- and solvo-metallurgical processes, will be critically reviewed with the view of opening a discussion on

the perspectives of their use in designing circular economy models in HM manufacturing as economically, technically and environmentally sustainable as possible.

## 1 Overview

Cemented carbides (CC), also referred to as hard-metals (HMs), are liquid-phase sintered composite materials consisting of at least one hard and wear-resistant phase (WC in the majority of cases) embedded in a soft and ductile metallic one. Even though it is possible to use Ni and Fe for corrosion resistance and low-performance application, respectively, Co is the most used binder metal in cemented carbides, despite its relatively high price<sup>1</sup>. Due to their unique properties of hardness, toughness and wear resistance, HMs are used in a wide range of applications, especially for cutting, drilling, smoothing, high wear-resistant parts, and crushing tools manufacturing<sup>2,3</sup>. These properties can be modulated by changing either the WC-Co composition and/or manufacturing processes<sup>4</sup>. The WC phase represents between 70 and 97 wt.% of the composite material, leaving the remaining 30-3 wt.% to the binder phase<sup>5</sup>. Additional properties can be conferred to the hard material by adding further alloying metals like Ti, Ta, and Nb in the forms of carbides<sup>4</sup>.

The manufacturing of HM tools and components is a complex powder metallurgical process, based on liquid phase sintering at temperatures in the 1350-1500 °C range<sup>2</sup>. Nowadays sintering usually takes place in sinterHIP furnaces, where, after an initial stage under vacuum, the consolidation process is assisted by hot isostatic pressing in the relatively low 25-100 bar range<sup>2</sup>. The sintered product is finished and in many cases coated by Chemical or Physical Vapour Deposition (CVD or PVD, respectively) of layers based on Ti (carbo-)nitrides and Al oxides and nitrides.

In many applications cemented carbides have replaced other materials such as tool steels, because they proved to be harder than high-speed and super-fast steel, withstanding higher cutting temperatures (1000 °C compared to 600 °C) and therefore allowing higher processing speeds. The worldwide HM production in 1993 was around 20,000 tons and increased from 30,000 tons in 2000 to almost

60,000 tons in 2008, then over 78,000 tons in 2018, with an estimated turnover worth to be more than 10 billion euros. This production growth is mainly due to the entry of China into the market. Specifically, from 2000 to date, the production in China raised from 7,000 tons in 2001 to 20,000 tons in 2011, up to 28,000 tons in 2017<sup>4</sup>.

Nowadays, China and Western Europe are both the major producers and consumers of WC in the world, with a production of 27% and 29%, respectively, and a consumption of 33% for both<sup>6</sup>.

## **2 Critical metals and circular economy in HM industrial sector**

As mentioned before, W and Co are the most employed raw materials for HM manufacturing given the key properties they may impart to the final material.

Tungsten is a heavy and refractory metal with unique physical and mechanical properties like high boiling and melting points, high density, good corrosion resistance, and good thermal and electrical conductivity<sup>7</sup>. In its raw form, tungsten is a hard steel-grey metal that is often brittle and hard to work and which resists attack by oxygen, acids, and alkalis<sup>8</sup>. For this reason, though the most important use of tungsten is in cemented carbide tools, it is also a key element for other industrial applications like alloyed steels and superalloys, mill products, X-ray tubes and lighting applications<sup>9,10</sup>.

China dominates the global mine production of tungsten with over 80% of the 78,400 tons produced in the world. Moreover, China holds the largest reserves of tungsten ores (~1,900,000 tons, corresponding to about 50% of worldwide deposits)<sup>11</sup>.

Tungsten carbide, WC, the main W-derivative used for HM manufacturing, is characterized by high thermal and electrical conductivity. It is generally prepared by carburizing W with C powder (in the form of carbon black) in an amount slightly higher than the 1:1 stoichiometry. The powder mixture is passed through induction or resistance furnaces in a controlled atmosphere at temperatures higher than 1500 °C. The granulometry of the carbide depends on that of the starting tungsten and carburization conditions and it generally falls in the nano-to-10 micron range<sup>9</sup>.

Cobalt is a key metal as a binder for HM production due to its unique property of high solubility of WC and formation of a eutectic with WC<sup>12</sup>. Cobalt is a ferromagnetic metal, stable at ambient conditions. Pure cobalt does not occur in nature but is present in several minerals and it is normally produced as a by-product of copper or nickel mining operations<sup>13</sup>. The Democratic Republic of Congo is the world's leading supplier of cobalt with about 70% of the world's mining production. Concerns has recently grown about handmade cobalt mining in armed conflict areas. However, the leading producer of refined cobalt is China which also holds the record as the world's largest consumer<sup>11</sup>. Cobalt supply is strongly influenced by economic contingency and industrial demand by application. Cobalt supply has significantly increased in recent years especially due to its use in lithium ions batteries (LIBs) which are widely employed in electronic consumer equipment as well as in hybrid and electric vehicles. The battery demand covered around 57% of the global use for cobalt in 2020 and it is set to continue growing<sup>14</sup>.

Current developments in the field of HMs are mainly related to the high and volatile prices of W and Co due to the difficult access to raw materials. Figure 1 shows the trend of W and Co prices in the last decade.

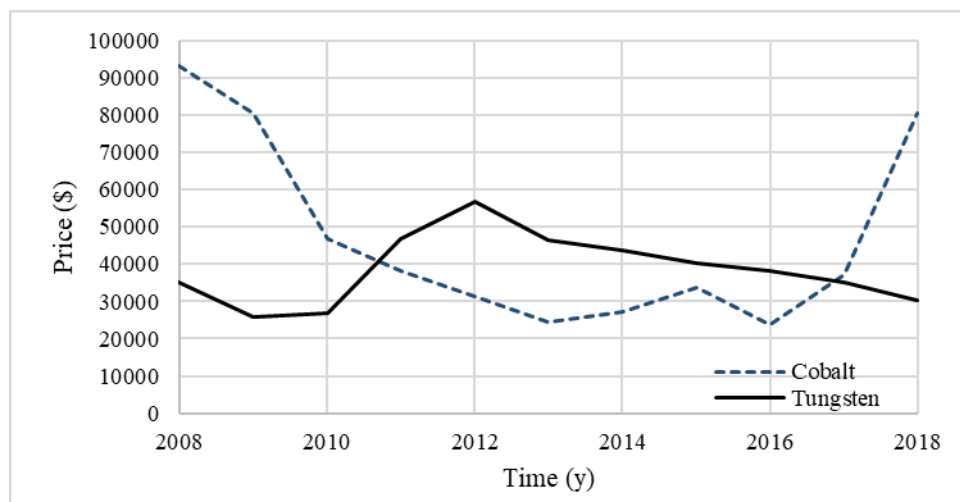


Figure 1 – Tungsten and Cobalt price in time (reported data as estimated by Metalary<sup>15</sup>).

Due to their economic relevance combined with the high risks related to the supply chain, in 2010 Co and W were included in the list of *Critical Raw Materials* (CRM) by the European Commission<sup>16,17</sup> and are nowadays considered critical elements of global importance<sup>18</sup>.

The growing concern of the industrialized countries about the supply of resources, as well as the growing awareness of the urgency of measures to protect the environment, have recently stimulated new regulations. In this context, the European directives urge to extend the life cycle of goods, by avoiding the production of waste as much as possible, and to promote sustainable recycling processes and/or energy recovery from waste<sup>19,20</sup>.

The economy is therefore being pushed to move from the linear model to the circular economy model, “a regenerative system in which resource input and waste, emission, and energy leakage are minimized by slowing, closing, and narrowing material and energy loops”<sup>21</sup>. The transition is not limited to certain materials or sectors. It is a systemic change that affects the entire economy and all products and services.

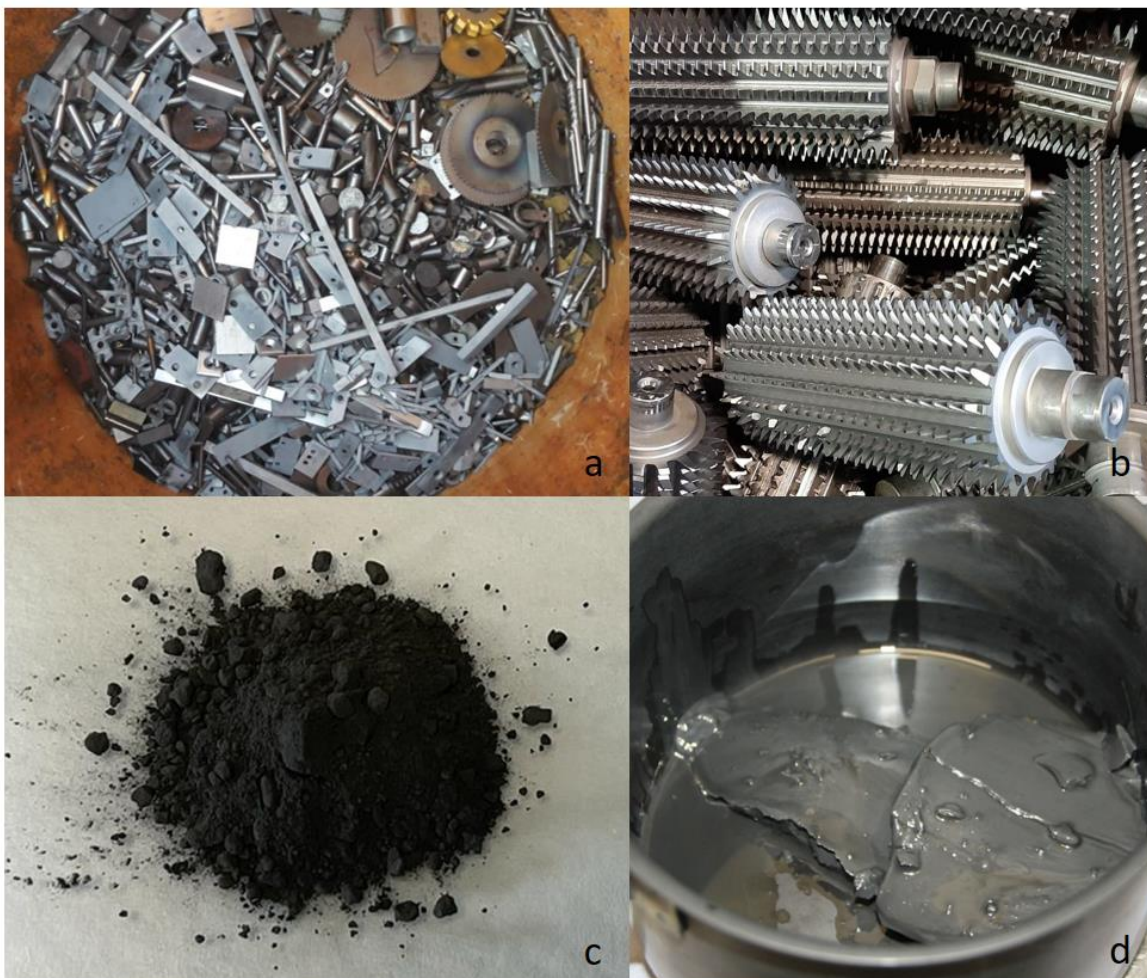
Fortunately, a significant recovery of W and Co from manufacturing by-products and scraps for circularity is already a good practice in the HM industry, estimated in 46% of global recycling of tungsten carbides<sup>22</sup>. However, nowadays, it should be recognized as a goal, with the view to preserve natural resources and prevent the disposal of toxic metals<sup>23</sup>. In addition, more sustainable production and recycling processes should be pursued, as urged by measures of various governments to tackle climate change<sup>24</sup>.

In this context, the present paper will review critically the different industrial approaches to the recovery and recycling of HM wastes, with specific reference to the role of bio-based organic acids in hydro- and solvo-metallurgical processes, as well as the perspectives of their use in the design of circular economy models, as economically, technically and environmentally sustainable as possible.

Indeed, peculiar chemical properties make organic acids suitable for gentle and effective metal leaching processes involving reagents which can be obtained by renewable biomass transformation avoiding carbon-based industrial processes.

### 3 Industrial approaches to HM wastes recycling

Recycling plays a key role in the development of a sustainable economy. A variety of tungsten carbide recycling technologies were developed over the last century for different WC-Co-based scraps. These secondary sources are typically represented by HM end-of-life tools and production rejects (named *hard scraps*) as well as by-products and residues of the manufacturing process with a not defined shape (e.g. wires, turnings, powders and sludge, named *soft scraps*) (See Figure 2)<sup>25</sup>. Because of their different shape and structure, direct or chemical recycling processes can be opportunely adopted for industrial purposes.



**HARD SCRAPS**

**SOFT SCRAPS**



Figure 2 – A selection of different types of hard and soft scraps. a) and b) examples of end-of-life HM tools; c) WC-based waste powders; d) HM manufacturing sludge.

### 3.1 Direct processes

Direct processes (Figure 3) consist of a series of chemical and/or physical treatments able to destroy the hard structure of the scrap, addressing the recovered materials to the same manufacturing sector of the treated scraps. These processes - i.e. molten Zn, cold stream, oxidation/reduction and menstruum processes<sup>26</sup> - are typically used for treating *hard scraps*. They mostly involve cleaning, sorting, debrazing and decoating HM scraps, then their treatment at high temperatures.

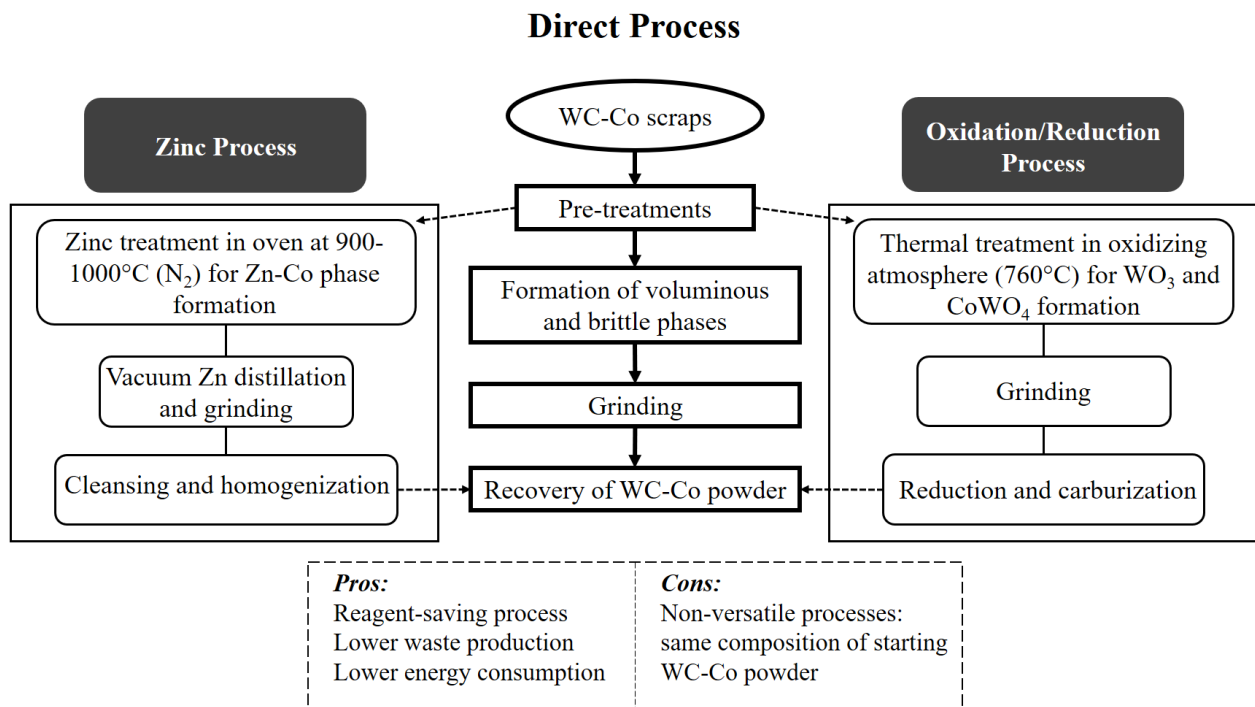


Figure 3 – Scheme (central column) and examples (lateral columns) of HM direct recycling processes.

Despite their ease of operations, direct processes suffer from several critical aspects related to the composition of the starting material. Indeed, the insufficient sorting or cleaning of the scraps will directly affect the quality of the ready-to-press (RTP) powder and the subsequently sintered HM part. On the other side, these processes are mostly non-versatile in tuning material composition, leaving the W:binder ratio unchanged. Direct processes are also limited by the size of the scraps: a dimensional reduction is often required to recycle unreacted parts for a new charge. Moreover, high-binder grades (up to 30% binder) scraps are not optimal candidates for this kind of processing, as significant sintering of the binder can occur. As a consequence, the range of suitable scraps to be treated by this approach is still limited<sup>27,28</sup>.

Despite these drawbacks, the lower requirement for energy and chemicals with respect to chemical recycling makes direct methods a valued alternative when the recycled products are addressed to feed HM manufacturing plants.

### **3.2 Chemical recycling**

Chemical recycling involves a multiphase intimate chemical transformation of the scraps, coupling thermal with chemical treatments, into intermediate products that are treated to obtain pure metals. As schematized in Figure 4, the most common chemical processes are based on the use of highly reactive alkaline treatments. Indeed, chemical processes can convert tungsten into “virgin” APT (ammonium paratungstate) or  $\text{Na}_2\text{WO}_4$ , high-purity intermediates most suitable for the production of tungsten compounds at the industrial level, as already well-known treating tungsten concentrates.

Oxidation/alkaline digestion currently represents the main chemical recycling approach in large manufacturing plants. It can be well integrated into plants originally built to convert raw materials into high-purity tungsten products. The resulting W and WC powders have the same properties as those from concentrates and can be applied for a variety of industrial applications. Details on the conventional chemical processes are hardly available in the literature.

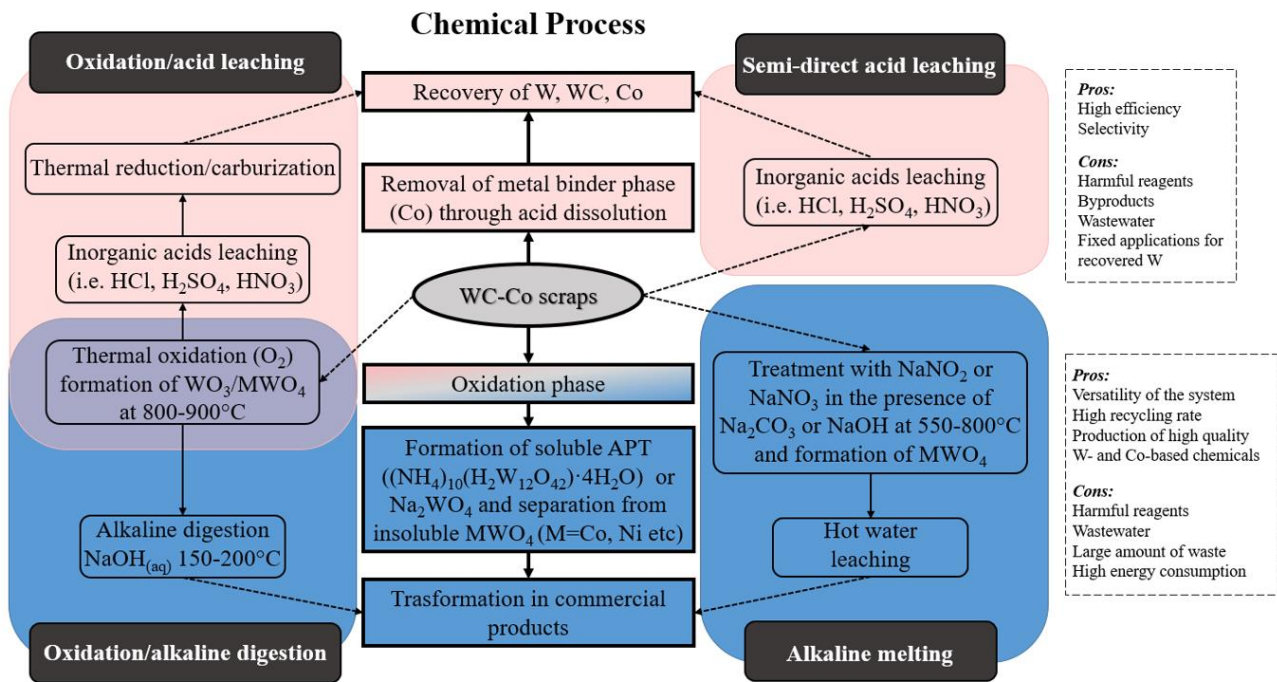


Figure 4 – Scheme (central column) and examples (lateral columns) of HM chemical recycling processes under acid (above part in pink) and alkaline (bottom part in blue) conditions.

A more selective chemical treatment may be represented by acid leaching which can be performed on both WC-based scraps and oxidized materials (see Figure 4). In both cases, the recycled fractions are typically addressed to the same applicative manufacturing field of the treated scraps. WC-based scraps may undergo acid leaching in inorganic acid solutions, which provides the selective binder metal dissolution leaving the WC phase almost unaffected, ready for a subsequent reuse (Semi-direct process). Differently, in the materials which undergo oxidation pre-treatments,  $\text{CoWO}_4$  dissolves in strong inorganic acid solutions, while  $\text{WO}_3$  remains almost undissolved. For HM manufacturing re-employment,  $\text{WO}_3$  needs to be reduced and carburized. In both cases, further treatments are required to recover cobalt from the leaching solution. The latest developments of the acidic hydrometallurgical leaching processes reported in the literature are summarized in Tables 1 and 2, for WC-Co-based scraps without and with oxidation pre-treatments, respectively.

Table 1 – Published inorganic acid leaching treatments on WC-Co scraps.

Acid	Scrap type*	Specimen characterization	Operational conditions						Optimal conditions	Results	Comments	Refs
			Concentration [M]	Liquid-to-solid ratio [mL/g]	Temperature [°C]	Added Oxidant	Reaction time [h]	Stirring [rpm]				
Nitric	HS	WC-Co chips; size: $\phi 10 \times 3$ mm <sup>3</sup> containing coarse WC grain (1-5 $\mu$ m) and 20 wt.% Co	1-3	-	130-200	-	6-72	-	3 M, 150 °C, 24 h	98% of Co leaching and complete oxidation of WC	Temperature higher than 170 °C forms CoWO <sub>4</sub> (insoluble). Co-recovery through electrowinning. WC recovery through reduction and carburization	Gao et al., 2005 <sup>29</sup>
	HS	WC-Co chips; size: $\phi 10 \times 3$ mm <sup>3</sup> containing fine WC grain (0.5-1 $\mu$ m) and 13 wt.% Co	1-13	-	170	-	24-240	-	1) 7 M, 170 °C, 24 h 2) 4 M, 170 °C, 144 h 3) 5 M, 170 °C, 48 h	Complete oxidation of WC	Conditions 2 and 3 require periodical (24h) manual scraping of the oxidized surface layer	
	HS	WC-Co insert; size: 12x12x4 mm <sup>3</sup> containing medium	0.5	-	50	H <sub>2</sub> O <sub>2</sub> (5M)	4	200	0.5 M, 50 °C,	Selective Co leaching	Cobalt dissolution occurs on surfaces	Kücher et al., 2018 <sup>30</sup>

		WC grain and 6 wt.% Co							H <sub>2</sub> O <sub>2</sub> (5 M), 4 h		up to 220 µm. Without H <sub>2</sub> O <sub>2</sub> no significant results	
	HS	WC-Co chips; size: φ15x5 mm <sup>3</sup> containing coarse WC grain (1-5 µm) and 20 wt.% Co	1.0	-	110	-	24	-	1 M, 110 °C, 24 h	25% of Co leaching	Passivation by WO <sub>3</sub> formation	Kojima et al., 2005 <sup>31</sup>
	P	Size: <90 µm containing 8.14 wt.% Co	0.5-1.5	10-20	25-70	-	2	900	0.5 M, 10 mL/g, 25 °C, 2 h, 900 rpm	91.5% of Co leaching	Cobalt can be recovered by precipitation adding NaOH, thermal calcining and hydrogen reduction or using USP (ultrasonic spray pyrolysis)	Gurmen et al., 2005 <sup>32</sup>
	P	Size: 250-90 µm containing 8.14 wt.% Co	0.5	10	25	-	2	900	0.5 M, 10 mL/g, 25 °C, 2 h, 900 rpm	68.5% of Co leaching		
	HS	13 wt.% Co	3-20% v/v	-	40-80	-	0.17-1.3	-	10% v/v, 10 kA/m <sup>2</sup> , 55-60 °C	-	The addition of cobalt, ammonium nitrate or potassium perchlorate improves WC oxidation	Madhavi Latha and Venkatachalam, 1988 <sup>33</sup>
Sulphuric	HS	WC-Co chips; size: φ15x5 mm <sup>3</sup> containing coarse WC grain (1-5 µm) and 20 wt.% Co	0.5	-	110	-	24	-	0.5 M, 110 °C, 24 h	35% of Co leaching	No oxidation of WC	Kojima et al., 2005 <sup>31</sup>

	HS	WC-Co chips; medium WC grain (1.13±0.2 µm) and 5.28 wt.% Co	1.0	10	75	-	252	500	1 M, 10 mL/g, 75 °C, 252 h	99.6% of Co leaching	Tungsten oxides slow down the Co leaching	Shemi et al., 2018 <sup>7</sup>
	P	9.59 wt.% Co	0.5-2	-	-	-	2	300	0.5 M, 2 h, 300 rpm	98.4% of purity of recovered WC; 98.07% purity of recovered Co	Cobalt leaching with ball milling. Cobalt recovery with Co(OH) <sub>2</sub> precipitation and subsequent reduction to obtain metallic cobalt powder	Lee et al., 2021 <sup>34</sup>
Hydrochloric	HS	WC-Co inserts; size: 12x12x4 mm <sup>3</sup> containing medium WC grain and 6 wt.% Co	1	-	50	H <sub>2</sub> O <sub>2</sub> (5M)	4	200	1 M, 50 °C, H <sub>2</sub> O <sub>2</sub> (5 M), 4 h	Selective Co leaching	Cobalt dissolution occurs on surfaces up to 245 µm. Without H <sub>2</sub> O <sub>2</sub> no significant results	Kücher et al., 2018 <sup>30</sup>
	HS	WC-Co chips; size: φ15x5 mm <sup>3</sup> containing coarse WC grain (1-5 µm) and 20 wt.% Co	1-6	-	80-200	-	24	-	6 M, 110 °C, 24 h	85% of Co leaching	WC no damage, but η phase formation	Kojima et al., 2005 <sup>31</sup>
	HS	Expose area 10x10 mm <sup>2</sup> ; 8-20 wt.% Co	0.5-2	-	25-70	-	37 (d)	-	1 M	Complete Co leaching	Recovery of WC particle with a regular shape and Co at the same time	Sun et al., 2019 <sup>35</sup>

	HS	WC-Co inserts; size: 12.75x12.75x3.75 mm <sup>3</sup> containing coarse WC grain (1 μm) and 6 wt.% Co	1-7 M	-	30-80	-	36	15	7 M, 80 °C, 36 h, 15 rpm	Complete Co leaching	Co-leaching improves increasing concentration and temperature	Wongsisa et al., 2015 <sup>36</sup>
	HS	Expose area 10x10 mm <sup>2</sup> ; coarse WC grain (2-4.5 μm) and 6-22 wt.% Co	0-5	-	25	-	-	-	1-3 M, 0.1 M citric acid addition, 25 °C	-	Citric acid addition improves Co dissolution	Lin et al., 1996 <sup>37</sup>
Phosphoric	HS	Expose area 10x10 mm <sup>2</sup> ; coarse WC grain (2-4.5 μm) and 6-22 wt.% Co	2	-	25	-	-	-	2 M, 0.4 M ammonium chloride addition, 25 °C	-	Ammonium chloride addition improves Co dissolution	Lin et al., 1996 <sup>37</sup>
	HS	Surface area 1-2 cm <sup>2</sup> ; 6 wt. % Co	1.25	-	-	-	-	-	1.25 M	Dissolution of Co-W	Selective dissolution of Co-W leaving WC unaffected	Malyshev and Hab, 2004 <sup>38</sup>
	HS	WC-Co inserts; size: 12x12x4 mm <sup>3</sup> containing medium WC grain and 6 wt.% Co	2.3	-	50	H <sub>2</sub> O <sub>2</sub> (5 M)	4	200	2.3 M, 50 °C, 4 h, H <sub>2</sub> O <sub>2</sub> (5 M)	Selective Co leaching	Cobalt dissolution occurs on surfaces up to 105 μm. Without H <sub>2</sub> O <sub>2</sub> no significant results	Kücher et al., 2018 <sup>30</sup>
Aqua regia	S	Size: <710 μm containing 5.99 wt.% Co	25-100 vol%	150 g/L	25-100	-	0.25-1	-	100 vol%, 150 g/L, 100 °C, 1 h	Complete Co leaching	Formation of tungstic acid. Recovery of W through crystallization of APT	Lee et al., 2011 <sup>39</sup>

\*Scrap type: HS = Hard Scrap; P = Powder; S = Sludge.

Table 2 - Published inorganic acid leaching treatments on oxidated WC-Co scraps.

Acid	Specimen characterization	Thermal Oxidation [°C] and pre-treatments	Operational conditions						Optimal conditions	Results	Comments	Refs
			Concentration [M]	Powder/Liquid [g/L]	Temperature [°C]	Added Oxidant	Reaction time [h]	Stirring [rpm]				
Sulphuric	9% Co in WC-Co scrap	900 °C for 3h; ball milling up to $\phi = 2-3 \mu\text{m}$	1-9	5	20-70	without and with H <sub>2</sub> O <sub>2</sub> (2 vol.%)	12-72	0-200	1) from 1 (72 h) to 9 M (12 h), 20 °C, 0 rpm 2) 1 M, 20 °C, H <sub>2</sub> O <sub>2</sub> , 56 h, 0 rpm	Complete Co leaching	Influence of stirring, oxidant, temperature and concentration	Kim et al., 2014 <sup>40</sup>
		900 °C for 3h	1-9	5	20	H <sub>2</sub> O <sub>2</sub> (2 vol.%)	10-18	200	1 M, H <sub>2</sub> O <sub>2</sub> (2% vol), 20 °C, 200 rpm, 150 g of Al <sub>2</sub> O <sub>3</sub> balls	Complete Co leaching	Simultaneous milling and Co dissolution; the use of alumina balls may cause contamination	
	9% Co in WC-Co scrap	900 °C for 3h; ball milling up to $\phi = 2-3 \mu\text{m}$	1	50	20	H <sub>2</sub> O <sub>2</sub> (2 vol.%)	24	200	1 M, 20 °C, H <sub>2</sub> O <sub>2</sub> , 24 h, 200 rpm	53% of Co leaching	Adding H <sub>2</sub> O <sub>2</sub> increases Co dissolution	Seo and Kim, 2016 <sup>41</sup>



As shown in the summarizing tables, Gao et al. carried out hydrothermal oxidation with nitric acid (HNO<sub>3</sub>) on sintered WC-Co HM parts with different WC granulometry and cobalt content (i.e. from WC grain size 1-5 μm and 20 wt.% Co to WC grain size 0.5-1 μm and 13 wt.% Co). The reported experiments showed that leaching efficiency is lower in the case of samples with smaller grain sizes and lower cobalt content. During the experiment, passivation on the surface of the specimen occurs due to the formation of tungstic acid<sup>29</sup>. The tungstic acid formation is the main drawback of the use of strong oxidizing acids like nitric, sulphuric and phosphoric, which hampers to achieve high dissolution rates of cobalt even in mild operative conditions<sup>31</sup>. On the other hand, chloric acid demonstrated to prevent oxidation phenomena when used in absence of a more oxidative environment, still rising safety concerns for the use of high concentration (6 M) hot (110 °C) strongly acidic solutions<sup>31</sup>. Differently, when highly oxidative operative conditions, such as the addition of H<sub>2</sub>O<sub>2</sub>, are used for improving efficiency, several oxidized W-based species have been identified. Specifically, Kücher et al. reported that high ORP (oxidation-reduction potential), related to increasing feeding rates of H<sub>2</sub>O<sub>2</sub>, at acidic pH, makes the initial dissolution rate faster and the chemically controlled reaction proceeds without significant slowdown. Nevertheless, furtherly increasing the oxidation potential (i.e. the feeding rate of H<sub>2</sub>O<sub>2</sub>), a W-oxide barrier is formed which reduces the reaction rate over time or even stops it completely<sup>42</sup>.

Table 1 shows also that the leaching of *soft scraps* takes a shorter reaction time with respect to *hard scraps* of similar composition, thanks to a higher contact surface exposed to the leaching solution. Accordingly, high efficiency is obtained using the same inorganic acids (i.e. nitric) under milder operative conditions<sup>32,39</sup>.

Among the cooperative treatments able to assist Co-leaching while keeping mild the experimental conditions, wet ball milling processes in an acid environment have been also tested by Lee et al. (2021)<sup>34</sup>. Specifically, high-purity WC was obtained as a residual powder after 2 h of a planetary ball milling process in an HM jar, when WC-Co sludges were milled with HM balls (wt. balls:powder

5:1) in the presence of 0.5 M H<sub>2</sub>SO<sub>4</sub>. As a further effect, WC particle size was reduced during ball milling and Co powder was obtained by precipitation in an alkaline environment and following reduction with H<sub>2</sub> [34]. A significant leaching rate on HM jars and balls is expected and should be taken into account in the cost analysis of the process.

A further approach based on the use of electro-dissolution processes has been recently developed with promising results<sup>6</sup>. Specifically, WC-Co scraps may undergo single-step electro-leaching processes in acidic (by HCl, HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub>) or alkaline (by NaOH, NH<sub>3</sub>) media providing very pure outcomes as compared to the other recycling methods. During anodic dissolution, the oxidation of WC-Co occurs at the anodic electrode producing the tungstate anion (WO<sub>4</sub><sup>2-</sup>) and cobalt cation (Co<sup>2+</sup>, <sup>3+</sup>) depending on the electrolyte and the presence of complexing additives. In the acidic medium, Co dissolves selectively while WC remains undissolved. In the alkali media, instead, both cobalt and WC go into solution forming soluble species. Subsequently, the Co deposits on the cathode. The main drawback of this process is still represented by passivation phenomena (by oxide and hydroxide films in acidic and alkaline environments respectively) occurring at the electrode during anodic dissolution, which lowers the effectiveness of the process hampering the electro-dissolution. Additives, such as organic acids (e.g. citric acid), were demonstrated to be suitable to obviate the constraint of passivation of the anode, reasonably through the formation of stable metal complexes into solution.

On the other side, WC-Co materials which underwent oxidative pre-treatments, are typically involved in milling and chemical treatments. Due to the inertness of the calcined material, just a few examples of leaching with inorganic acids are reported in the literature (see Table 2) and highlight the fundamental effect of a combined mechanical-chemical approach with respect to a sequence of grinding and chemical leaching treatments. Specifically, sulphuric acid solutions were used as leaching agents, without and with H<sub>2</sub>O<sub>2</sub> addition: 1) after material grinding; 2) by wet milling in plastic jars loaded with ZrO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> balls, with simultaneous grinding and Co dissolution<sup>40,41,43</sup>.

A quantitative  $\text{CoWO}_4$  leaching was indeed obtained with 1 M sulphuric acid solutions in the presence of  $\text{H}_2\text{O}_2$  at 20 °C within 56 and 18 hours respectively in cases 1) and 2). These findings demonstrate wet milling heavily improves efficiency in Co dissolution due to the repetitive impact of the material with balls which impels the chemical reaction. The attrition also prevents  $\text{CoWO}_4$  passivation by tungstic acid, with  $\text{H}_2\text{O}_2$  which contributes to converting  $\text{WO}_3 \cdot \text{H}_2\text{O}$  in the more soluble peroxo-tungstic acid  $\text{WO}_3 \cdot \text{H}_2\text{O}_2 \cdot \text{H}_2\text{O}$ . Despite the intrinsic interest in these relevant results, the use of zirconia/alumina balls could contaminate the product addressed to HM manufacturing, enriching it with unwanted elements. Different materials for ball milling should be identified and tested for this purpose.

As described, the use of a selective semi-direct method on cobalt is a good way for both *hard* and *soft* scraps, except for sludges because the solid residue contains impurities such as silica and other insoluble materials. Using an indirect method with an alkaline solution (NaOH) allows recovering the W as  $\text{Na}_2\text{WO}_4$ . Subsequently, the Co residue, typically in the form of hydroxide or oxide, can be leached with an acid treatment<sup>43,44</sup>.

Nowadays, chemical processes represent the most versatile and selective approach applicable to all sorts of W-based materials, such as *hard* or *soft scraps*, and achieving high-purity raw materials that can be used in all the desired fields. However, the main drawbacks include high energy and economic costs, the use of dangerous reagents and the production of a large amount of wastewater<sup>6</sup>.

To overcome these limitations, the use of safer and selective reagents and/or less energy-demanding processes ideally addressed to “zero-waste” production would be desirable in terms of environment and health preservation, over than fulfilling regulation requirements.

## 4 Bio-based organic acids: a valued alternative for selective leaching

In the described framework, the hydrometallurgical employment of bio-based organic acids is attracting increasing attention from researchers and companies as an alternative to the use of strong inorganic acids for the selective leaching of the binder from WC-based scraps. Indeed, unlike cobalt, WC typically shows negligible reactivity towards weak non-oxidizing acids. Moreover, W redox and coordination chemistry are poorer than those shown by Co, where both +2 and +3 oxidation numbers are common, characterized by a variety of different coordination numbers and geometries depending on the solvent as well as the steric hindrance and strength of the ligands. In this context, selective Co-leaching seems to be impelled if appropriate complexing/oxidizing species are selected. On the other side, due to the peculiar complexing capabilities in their deprotonated forms, organic acids may represent an appealing alternative to strong inorganic bases in leaching metals from  $\text{WO}_3$ -based materials, as summarized in Figure 5.

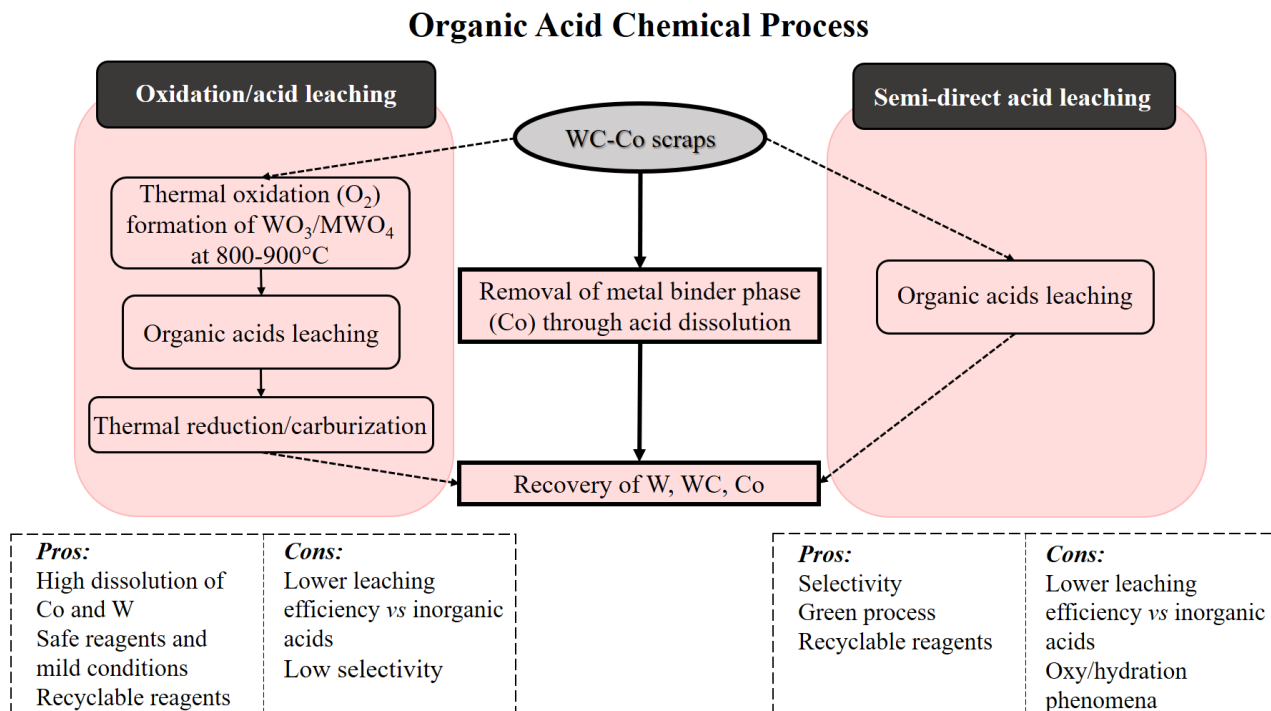


Figure 5 – Scheme (central column) and examples (lateral columns) of HM organic acid chemical recycling processes.

## 4.1 Bio-derived organic acids tested for metal leaching

A selection of easily available, renewable, cheap and safe organic acids promising for metal leaching purposes should take into account their acidity (expressed as  $pK_{a1}$  values) and solubility in water (as well as in other *green* solvents like ethanol). Furthermore, species containing carboxylic groups seem particularly appealing due to their complexing/chelating capabilities in their deprotonated form, favouring metal oxidation and leaching. In this framework, organic acids with these features already reported in the literature as leaching agents for Co- and W- containing species in HM manufacturing sector, are following described. Indeed, promising results have been obtained in the last decade, highlighting the high potential of organic acids as leaching agents towards metals contained in a variety of substrates<sup>45</sup>.

Currently, commercial production of organic acids relies primarily on chemical conversions of precursors from petroleum processing. Nevertheless, biological production from organic by-products and waste streams could play a pivotal role as an alternative that pursues circular bio-economy goals<sup>46</sup>. Moreover, the use of these renewable and widely available substrates stimulates the transition toward innovative and environmentally friendly strategies for waste valorisation, besides the more conventional ones. On the other side, the heterogeneous nature of these substrates may affect processes and costs for obtaining high-purity chemicals and open the way to the use of less purified organic acid mixtures able to preserve leaching capabilities by low operative and environmental costs.

### 4.1.1 Acetic acid

Acetic acid was obtained by distillation from vinegar in 1700 by the German chemist Georg Ernst Stahl. Acetic acid is considered a commodity chemical for a variety of end-user industries (textile, fibre, pharmaceutical, foods, etc.)<sup>47</sup>. The global demand for acetic acid was estimated to be 16.1 Mt in 2020, and it is projected to reach 19.6 Mt by 2027, with a compound annual growth rate (CAGR) of around 3% for the period 2020–2027<sup>47</sup>. Currently, about 75% of acetic acid is produced industrially via the carbonylation of methanol using syngas (primarily formed by CO and H<sub>2</sub>). On the other hand,

biological acetic acid production from bacteria has several advantages in terms of the lowest costs<sup>48</sup>. Acetogenesis (i.e. reducing CO<sub>2</sub> to acetate by *Clostridium aceticum*, *Acetobacterium woodii*, *C. thermoaceticum*, *Thermoanaerobacter kivui* and *A. wieringae*), acetic fermentation (i.e. aerobic conversion of a carbohydrate-source through ethanol by-production catalysed, among others, by *Acetobacter*, *Acidomonas*, *Ameyamaea*, *Gluconacetobacter*, *Gluconobacter*) and yeast fermentation (by *Candida stellata*, *Kloeckera apiculata* or the genus *Brettanomyces/Dekkera*) are the three main acetic acid biological production processes.

#### 4.1.2 Succinic acid

Succinic acid was purified for the first time from amber by Georgius Agricola in 1546<sup>49</sup>. It is a four-carbon dicarboxylic acid that plays an important role as a precursor molecule in the synthesis of biodegradable polyester resins, dyestuffs and pharmaceuticals, and as an additive in the food industry<sup>50</sup>. Today, succinic acid is produced exclusively from crude oil by catalytic hydrogenation of maleic anhydride to succinic anhydride and subsequent hydration or by direct catalytic hydrogenation of maleic acid. The potential market for succinic acid itself and its derivatives is estimated to be more than 270,000 t/y, while the market price for petrochemically produced succinic acid is about 5.9–8.8 USD/kg depending on purity. The raw material costs, based on production from maleic anhydride, are about 1 USD/kg succinic acid<sup>50</sup>. As an alternative, Song H. et al. reported that various microorganisms have been used to produce succinic acid from different carbon sources, namely *Anaerobiospirillum succiniciproducers* and *Actinobacillus succinogenes* growing on galactose, galactose/glucose, and galactose/lactose<sup>49,51</sup>. Pakchamni et al. produced around 40 g/L of succinic acid from pre-treated sugarcane trash inoculated with *Actinobacillus succinogenes*<sup>52</sup>.

#### 4.1.3 Lactic acid

Lactic acid was first discovered in sour milk in 1780 by the Swedish chemist C. W. Scheele<sup>53</sup>. It is a naturally occurring  $\alpha$ -hydroxy acid. It is a chiral molecule, consisting of two enantiomers, the L-(+)-lactic acid (or (S)-lactic acid) and the D-(–)-lactic acid (or (R)-lactic acid)<sup>54</sup>. The (S)-enantiomer is obtained from anaerobic glycolytic catabolism. Päivi Mäki-Arvela et al.<sup>55</sup> reported that lactic acid can

be converted into different useful chemicals such as acrylic acid, pyruvic acid, propylene glycol, 1,2-propanediol, 2,3-pentanone, becoming widely appealing for food, pharmaceutical, cosmetic, chemical and textile industries<sup>56</sup>. Its importance has recently grown up thanks to its use as a monomer in biopolymers such as polylactic acid (PLA)<sup>57</sup>. For these reasons, the global lactic acid market required 1,220 kt in 2016 and is expected to expand at a CAGR of 8.0% from 2021 to 2028<sup>58-60</sup>. Lactic acid can be produced in its racemic form by chemical synthesis from coal or oil through the reaction of acetaldehyde with hydrogen cyanide to give lactonitrile and subsequent hydrolysis of the intermediate acetonitrile catalysed by strong acids<sup>61</sup>. However, up to 90% of commercial lactic acid is produced through the fermentation of sugars, mainly glucose and sucrose, utilizing Lactic Acid Bacteria (LAB), such as *Lactobacillus* strains<sup>53</sup>. Alves de Oliveira et al. reported a number of promising renewable feedstock such as cassava starch, corn starch, fresh sweet potato, sugarcane molasses and bagasse, white rice bran, corn stover, paper sludge, green algae, mango peel, coffee residues, and whey<sup>58</sup>.

#### **4.1.4 Itaconic acid**

Itaconic acid was discovered by S. Baup in 1837 as a product of the thermal decomposition of citric acid<sup>62</sup>. Later, it was produced from *Aspergillus itaconicus* in 1931 by Kinoshita<sup>63</sup>. Nowadays, the industrial production of itaconic acid is based on a thermochemical approach, i.e. the pyrolysis of citric acid to itaconic anhydride, followed by the hydrolysis of the anhydride, with a production of about 41,000 t/y and a world market of over 216 million USD in 2020<sup>63</sup>. However, other approaches have been investigated, such as those proposed by Dan Cristian Vodnar et al. through fermentation of lignocellulosic biomass mediated by *Aspergillus terreus* and *Ustilago maydis* strains or with metabolically engineered bacteria like *E. Coli* and *Corynebacterium glutamicum*<sup>63</sup>.

#### **4.1.5 Lactobionic and maltobionic acids**

Lactobionic and maltobionic acids are patented  $\alpha$ -hydroxy acids belonging to the “bionic” family. Bionics are polyhydroxy acids (PHAs) with an additional sugar molecule attached to the PHA structure. Lactobionic acid was synthesized for the first time by Fisher and Meyer in 1889 as the oxidation product of the lactose-free aldehyde group after chemical oxidation with bromine i.e. produced by

chemical synthesis from refined lactose<sup>64</sup>. It can be also produced from whey by *Pseudomonas taetrolens*<sup>65</sup> or through the biological oxidation of lactose<sup>64</sup>. Maltobionic acid is a maltose-derived stereoisomer of lactobionic acid. Both these acids, display antioxidant, biodegradable, biocompatible and chelating properties that make them useful in different chemical fields, first of all in cosmetics and skin care fields<sup>64</sup>.

#### **4.1.6 Formic acid**

Formic acid was first synthesized from hydrocyanic acid by the French chemist Joseph Gay-Lussac. Formic acid is a simple, strong organic acid, that is widely used in agricultural, rubber, pharmaceutical, leather and textile industries or as a building block in various chemical syntheses<sup>66</sup>. In 2019, the annual global market for formic acid is about 620 million USD which would maintain a constant increase in the future. The current industrial production of formic acid involves a fossil-based process at high pressure (around 4 MPa). Inexpensive and readily available cellulosic biomass can be also used as the carbon source through chemical<sup>66</sup> or biological processes<sup>67</sup>.

#### **4.1.7 Malic acid**

Malic acid (2-hydroxybutanedioic acid) is used extensively in food, chemical, pharmaceutical and agricultural industries as well as in metal cleaning, textile finishing, water treatment, fabric dyeing or for the chemical synthesis of poly  $\beta$ -l-malic acid (PMA)<sup>68</sup>. The global market for DL-malic acid has recently been estimated at 60,000–200,000 t/y<sup>69</sup>. The main method of producing malic acid is the chemical synthesis route through the hydration reaction with petroleum-derived maleic acid or fumaric acid as the substrate. Microbial fermentation, which could synthesize pure L-malic acid from renewable raw materials such as lignocellulose mediated by *Aspergillus spp*, *Penicillium spp.*, *Zygosaccharomyces rouxii*, and *Ustilago trichophora* among others, has attracted great interest in recent years<sup>68</sup>.

#### **4.1.8 Citric acid**

Citric acid was first isolated from lemon juice imported from Italy by Karls Scheels in England in 1874. Later, in 1923, Wehmer observed the presence of citric acid as a by-product of calcium oxalate



produced by a culture of *Penicillium glaucum*<sup>70</sup>. Citric acid is a commodity chemical produced and consumed throughout the world. It is used mainly in the food and beverage industry, primarily as an acidulant, and its global production in 2007 was over 1.6 Mt<sup>71</sup>. Vandenberghe L. et al. reported that several microorganisms including bacteria, fungi and yeasts have been employed to produce citric acid such as yeasts *Saccharomycopsis sp.*, fungus *Aspergillus niger* by fermentation of glucose or sucrose<sup>70,72</sup>. Citric acid is known to be a biodegradable, eco-friendly, low-cost, safe and versatile chemical for sequestering, buffering, wetting, cleaning and dispersing.

#### **4.1.9 Tartaric acid**

Tartaric acid (2,3-dihydroxybutanedioic acid) is a naturally occurring dicarboxylic acid that was obtained in 1769 by the Swedish chemist Carl Wilhelm Scheele. Tartaric acid has applications in the textile printing, dyeing, pharmaceutical, and food industries<sup>73</sup> as well as in winemaking to adjust the initial pH of the must before fermentation. The global market value of tartaric acid reached a value of 215.7 million USD in 2017 and is expected to grow at a CAGR of 5.77%. Currently, tartaric acid is extracted from wine lees (the sludge that remains at the bottom of the wooden barrels at the end of both alcoholic and malolactic fermentation) or obtained by chemical synthesis with the reaction of maleic anhydride with hydrogen peroxide<sup>74</sup>.

#### **4.1.10 Maleic acid**

Maleic acid was first prepared in 1830, but its commercial production began in 1928. Maleic acid is an important intermediate in the chemical industry with a production of about 1,800,000 t/y, constantly increasing<sup>75</sup>. Besides the main industrial route of production from benzene<sup>76</sup>, maleic acid can be also easily synthesized from renewable resources based on catalytic oxidation of furfural in liquid media with oxygen<sup>77</sup>, by fungi such as *Aspergillus Niger* from renewable substrates<sup>76</sup> or synthesized through biomass-based feedstocks catalytic conversion<sup>78</sup>.

## 4.2 Bio-based organic acid leaching of WC-Co materials

In the described context, efforts have been spent on finding safe, selective but effective organic acids for binder leaching from HM scraps. This approach is based on the well-known complexing behaviour of the anions of carboxylic acids towards metals such as cobalt in their oxidated form<sup>79-81</sup>, in concert with the oxidative action played by H<sup>+</sup> towards negative reduction potential metals ( $E^{\circ}\text{Co}^{2+}/\text{Co} = -0.277\text{V}$ ). Typically, in the same conditions, WC and W are almost inert, allowing a highly selective binder dissolution process. Table 3 summarizes the results and process conditions reported in the literature about the treatment of WC-Co-based scraps with organic acid solutions.

Table 3 – Published organic acid leaching treatments on WC-Co scraps.

Acid	Scrap Type*	Specimen characterization	Operational conditions						Optimal conditions	Results	Comments	Refs
			Concentration [M]	Liquid to Solid ratio [L/kg]	Temperature ** [°C]	Added Oxidant	Reaction time [h]	Stirring [rpm]				
Acetic	HS	D Circuit board drill; size: $\phi$ 3x28 mm <sup>3</sup> containing fine WC grain (<0.5 $\mu$ m) and 7.9 wt.% Co	3.6 - 14	-	60-80	air/O <sub>2</sub> pressureless or 5 bar	50-300	-	8.7 M, 80 °C, 144 h, O <sub>2</sub> , 5 bar	Complete Co leaching	Increasing the grain size, the Co content, the T (from 40 to 80), and the pressure (up to 5 bar) results in an increased dissolution rate.	Edtmaier et al., 2005 <sup>82</sup>
	HS	J Cutting insert; size: 9.6x9.6x5 mm <sup>3</sup> containing medium WC grain (2 $\mu$ m) and 11 wt.% Co	3.6-5.3	-	40-80	-	300	-	5.3 M, 60 °C, 288 h, 80 L O <sub>2</sub> /h pressureless	Complete Co leaching		
	HS	EB30 Wear part; size: 12.6x12.6x3.1 mm <sup>3</sup> containing coarse WC grain (5.3 $\mu$ m) and 10% wt. Co	3.6-8.7	-	80	O <sub>2</sub> , 1-5 bar	-	-	8.7 M, 80 °C, 60 h, O <sub>2</sub> , 5 bar	Complete Co leaching		
	HS	BB40 Wear part; size: $\phi$ 8x20 mm <sup>3</sup> containing coarse WC grain (9.5 $\mu$ m) and 13 wt.% Co	8.7	-	80	O <sub>2</sub> , 5 bar	-	-	4.4 M, 80 °C, O <sub>2</sub> , 5 bar	Complete Co leaching		
	HS	TW Cutting insert; size: 19.5x19.5x4.75 mm <sup>3</sup> containing fine/medium WC grain (0.8-2 $\mu$ m) and 8-10 wt.% Co	3.6-14	-	80	-	50	-	3.6 M, 80 °C, 50 h	Selective Co leaching	299 $\mu$ m of leached layer thickness	

	HS	K Cutting knife; size: 1.5x11x350 mm <sup>3</sup> containing fine WC grain (0.5-0.65 μm) and 10-12 wt.% Co	3.6-14	-	80	-	50	-	14 M, 80 °C, 50 h	Selec- tive Co leach- ing	140 μm of leached layer thickness	
	HS	H Cutting insert; size: 25x14x4 mm <sup>3</sup> containing medium WC grain (2 μm) and 14.6 wt.% Co	3.6-14	-	40-80	O <sub>2</sub> , pressure- less	100	-	3.6 M, 80 °C, 50 h, O <sub>2</sub> pres- sureless	Selec- tive Co leach- ing	500 μm of leached layer thickness	
	HS	WC-Co insert; size: 12x12x4 mm <sup>3</sup> containing medium WC grain and 6 wt.% Co	3.5	-	50	H <sub>2</sub> O <sub>2</sub> (5 M)	4	200	3.5 M, 50 °C, H <sub>2</sub> O <sub>2</sub> (5 M), 4 h	Selec- tive Co leach- ing	Cobalt dissolution occurs on surfaces up to 100 μm; without H <sub>2</sub> O <sub>2</sub> no significant results	Kücher et al., 2018 <sup>30</sup>
	P	2-6 μm WC grain size; 73.88 wt.% W, 19.55 wt.% Co	0.5	500	r.T.	-	12	-	0.5 M, r. T., L/S=500 L/kg, 12 h	About 80% of Co leach- ing	Cobalt dissolution in 12 h	Oumarou, 2023 <sup>83</sup>
Formic	HS	WC-Co insert; size: 12x12x4 mm <sup>3</sup> containing medium WC grain and 6 wt.% Co	1.5	-	50	H <sub>2</sub> O <sub>2</sub> (5 M)	4	200	1.5 M, 50 °C, H <sub>2</sub> O <sub>2</sub> (5 M), 4 h	Selec- tive Co leach- ing	Cobalt dissolution occurs on surfaces up to 75 μm; with- out H <sub>2</sub> O <sub>2</sub> no signif- icant results	Kücher et al., 2018 <sup>30</sup>
Succinic	P	2-6 μm WC grain size; 73.88 wt.% W, 19.55 wt.% Co	0.5	500	r.T.	-	12	-	0.5 M, r. T., L/S=500 L/kg, 3 h	About 95% of Co leach- ing	Cobalt dissolution in 3 h	Oumarou, 2023 <sup>83</sup>
Lactic									0.5 M, r. T., L/S=500 L/kg, 3 h	About 95% of Co	Cobalt dissolution in 3 h	

										leaching		
Itaconic									0.5 M, r.T., L/S=500 L/kg, 4 h	About 95% of Co leaching	Cobalt dissolution in 4 h	
Lactobionic									0.5 M, r.T., L/S=500 L/kg, 4 h	About 95% of Co leaching	Cobalt dissolution in 4 h	
Citric									0.5 M, r.T., L/S=500 L/kg, 9 h	About 95% of Co leaching	Cobalt dissolution in 9 h	
Maleic	P	0.8-6 $\mu\text{m}$ WC grain size; 72.74 wt.% W, 20.40 wt.% Co	0.5-1 <sup>c</sup>	14-200	r.T.	-	16	-	0.5 M, r.T., L/S=14 L/kg, 6 h	Complete Co leaching	Lower Co dissolution occurs in samples with lower WC grain size	Oumarou et al., 2021 <sup>84</sup>
	P	2-6 $\mu\text{m}$ WC grain size; 73.88 wt.% W, 19.55 wt.% Co	0.5-1 <sup>c</sup>	14-200	r.T.	-	16	-	0.5 M, r.T., L/S=14 L/kg, 3 h	Complete Co leaching		
	P	2-6 $\mu\text{m}$ WC grain size; 73.88 wt.% W, 19.55 wt.% Co	0.5	500	r.T.	-	12	-	0.5 M, r.T., L/S=500 L/kg, 9 h	About 95% of Co leaching	Cobalt dissolution in 9 h	Oumarou, 2023 <sup>83</sup>

<sup>a</sup>Scrap type: HS = Hard Scrap; P = Powder; S = Sludge.

<sup>b</sup>Temperature: r.T. = room temperature.

°Solvent = Ethanol.

Specifically, Edtmaier et al. studied the behaviour of acetic acid aqueous solutions for the selective removal of the Co binder from HM scraps<sup>82</sup>. The goal of this study was the Co leaching from HM scraps of the original size, investigating the influence of process conditions. HM cutting knives (K) and inserts (J, TW, H), wear parts (EB30, BB40), circuit board drills (D) with different WC grain sizes (<0.5-9.5  $\mu\text{m}$ ) and Co content (7.9-14.6%), were used as test specimens. Preliminary leaching experiments addressed to investigate the effect of temperature, acid concentration and oxygen partial pressure with respect to the nominal composition of the scrap were performed in a thermostated glass batch reactor, where oxygen (or air) was bubbled through a bed of scrap pieces covered by aqueous acetic acid solution. The effect of oxygen (or air) pressure was specifically investigated in a thermostated pressure reaction vessel. During the treatment, the original shape of the scrap was maintained. Indeed, the leaching solution etched first the edges of the scrap and then approached the inner portion, leaving an “ash”-layer of WC and other carbides over the core of still unreacted WC-Co. The thickness of this leached layer was monitored in time as the indicator for Co removal. The study showed for all samples an increasing rate of Co dissolution with Co content, increasing temperature as well as partial oxygen and overall pressure. Also, a reduction in leaching times was observed in coarser WC grain samples in which penetration of the leaching solution is favoured concerning the finer ones. On the other hand, increasing acid concentration did not result in a higher dissolution rate. This behaviour is attributed by the authors to the formation, at these decreasing pH (up to 0.4 for 14 M acetic acid solution), of insoluble ultrafine tungstic acid which deposits in the pores of the matrix hampering the leaching reaction. Table 3 details the results obtained for the different treated types of scraps and specific reaction conditions. Referring to a test specimen consisting of a WC-(Ti,Ta,Nb)C-(10%)Co of 3 mm thickness, complete removal of the binder was achieved by acetic acid 3.6 M within about 5 days at 1 bar gauge pressure of pure O<sub>2</sub> and 80 °C temperature (about 2.5 days if the O<sub>2</sub> pressure is increased to 5 bars and the acid concentration increased to 8.7 M). In the reported conditions, also W, Fe, Cr and V present in the binder phase, were dissolved, leaving the nude WC-(Ti,Ta,Nb)C skeleton and obtaining a solution requiring selective steps for single metals recovery.

Investigations on organic acids' efficacy in leaching Co from WC-Co-based materials were also conducted by Kücher et al., using primarily formic and acetic acid aqueous solutions<sup>30</sup>. The work compares the behaviour of inorganic (such as nitric, hydrochloric and phosphoric acid) and organic acids, with and without the addition of oxidizing agents (such as H<sub>2</sub>O<sub>2</sub>, KMnO<sub>4</sub>), in leaching cutting inserts with 6 wt.% of Co content. As shown in Figure 6a, test specimens were made in conformity to ISO 1832 regulation and consisted of WC-Co portions (12x12x4mm) embedded into transparent non-conducting thermoplasts which expose only the 2/3 of one surface of the HM material to the leaching solution (being the remaining 1/3 covered by a cyanoacrylate-glye). This system enables the measurement of the worn substrate (the part that leaves the test specimen for the effect of the etching, see Figure 6b), as well as the depleted binder zone (the layer consisting of the only nude WC-based skeleton, Figure 6c, Zone 1) and the transition area (the underlying partially leached layer, Figure 6c, Zone 2). Reactions were performed in a 250 mL borosilicate double-walled vessel equipped with a reflux condenser, for 4 h at 50 °C, under N<sub>2</sub> atmosphere and magnetic bar stirring.

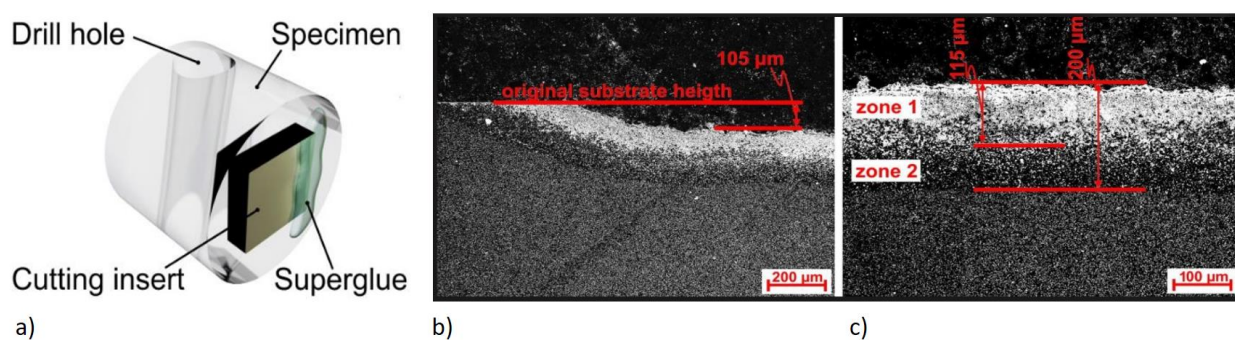


Figure 6 - a) 3D model of the test specimens; b) and c) exemplary dark field microscopy pictures of the layering occurring after leaching by acids (in the specific case with 0.5 M HNO<sub>3</sub>(aq) + 5 M H<sub>2</sub>O<sub>2</sub>(aq), 50 °C, 4 h) as discussed by Kücher et al.<sup>30</sup>, illustrating of the 105 µm worn substrate (b), evaluation of the Co-depleted and penetration depth with transition zone (c).



Based on the reported results, a direct comparison of the efficacy of the different acid solutions in Co-leaching can be hardly approached, due to the use of heterogeneous conditions between the experiments. Nevertheless, two main aspects have been pointed out:

- 1) the presence of an oxidizing species (such as  $\text{H}_2\text{O}_2$ ) in the reaction environment seems unavoidable to obtain significant progress in the Co leaching reaction with both inorganic and organic acid solutions;
- 2) organic acids displayed a more selective behaviour towards Co even if inorganic acids corroded a deeper layer.

With the view to widen the knowledge on the use of organic acids in this field, a systematic investigation of the Co-leaching properties of a series of bio-based organic acids in a water environment was recently approached<sup>83</sup>. The acids selection comprised a series of carboxylic organic acids having  $\text{pK}_{\text{a}1}$  values spanning in the 1.8-4.6 range and different coordination properties. Specifically, acetic ( $\text{pK}_{\text{a}1} = 4.56$ , HAc), succinic (3.99,  $\text{H}_2\text{Suc}$ ), lactic (3.67, HLac), itaconic (3.66,  $\text{H}_2\text{It}$ ), lactobionic (3.6, HLB), citric (2.90,  $\text{H}_3\text{Cit}$ ) and maleic (1.76, HMal) acid solutions, were tested as leaching agents for Co on WC-Co powders resulting from the shaping phases of the manufacturing process of HM tools. The experiments carried out on the cited samples highlighted the occurrence of the reactions summarized in Table 4, where the leaching may involve the oxidizing action of the organic acid (through the  $\text{H}^+$  ion reduction) and/or the oxidizing action of dissolved  $\text{O}_2$ , depending on the acidity of the lixiviant and the coordination properties of the deprotonated acids.

Table 4 - Leaching reactions occurred with WC-Co powders by selected organic acids aqueous solutions (0.5 M) at room conditions. Leaching times refer to  $\geq 95$ wt.% of Co dissolution<sup>83</sup>.

<b>Organic acids</b>	<b>Main leaching pathways found in water medium</b>	<b>Leaching Time (h)</b>
<b>HAc</b>	$2\text{Co(s)} + \text{O}_2(\text{g}) + 2\text{HAc}(\text{aq}) \rightarrow 2[\text{Co}(\text{HAc})(\text{H}_2\text{O})](\text{aq})$	>12
<b>H<sub>2</sub>Suc</b>	$\text{Co(s)} + \text{H}_2\text{Suc}(\text{aq}) + n\text{H}_2\text{O(l)} \rightarrow [\text{Co}(\text{Suc})(\text{H}_2\text{O})_n](\text{aq}) + \text{H}_2(\text{g})$ $2\text{Co(s)} + \text{O}_2(\text{g}) + 2\text{H}_2\text{Suc}(\text{aq}) + (n-2)\text{H}_2\text{O} \rightarrow 2[\text{Co}(\text{Suc})(\text{H}_2\text{O})_n](\text{aq})$	3
<b>HLac</b>	$2\text{Co(s)} + \text{O}_2(\text{g}) + 4\text{HLac}(\text{aq}) \rightarrow 2[\text{Co}(\text{Lac})_2(\text{H}_2\text{O})_2](\text{aq})$	3
<b>H<sub>2</sub>It</b>	$3\text{Co(s)} + \text{H}_2\text{IT}(\text{aq}) + 3n\text{H}_2\text{O(l)} \rightarrow [\text{Co}(\text{It})(\text{H}_2\text{O})_n]_3(\text{aq}) + \text{H}_2(\text{g})$ $6\text{Co(s)} + 3\text{O}_2(\text{g}) + 6\text{H}_2\text{IT}(\text{aq}) \rightarrow 2[\text{Co}(\text{It})(\text{H}_2\text{O})_n]_3(\text{aq}) + (6-3n)\text{H}_2\text{O(l)}$	4
<b>HLB</b>	$2\text{Co(s)} + \text{O}_2(\text{g}) + 4\text{HLB}(\text{aq}) \rightarrow 2[\text{Co}(\text{LB})_2(\text{H}_2\text{O})_2](\text{aq})$	4
<b>H<sub>3</sub>Cit</b>	$3\text{Co(s)} + 2\text{H}_3\text{Cit}(\text{aq}) + n\text{H}_2\text{O(l)} \rightarrow [\text{Co}_3(\text{Cit})_2(\text{H}_2\text{O})_n](\text{s}) + 3\text{H}_2(\text{g})$	9
<b>H<sub>2</sub>Mal</b>	$\text{Co(s)} + 2\text{H}_2\text{Mal}(\text{aq}) + 4\text{H}_2\text{O(l)} \rightarrow [\text{Co}(\text{HMal})_2(\text{H}_2\text{O})_4](\text{s}) + \text{H}_2(\text{g})$	9

As shown, maleic and citric acids, characterized by the lowest  $\text{pK}_{\text{a}1}$  values, combine complexing and oxidizing actions, while with the other tested acids the dissolved oxygen assists the leaching as oxidizing species, as already pointed out by Edtmaier et al. in the case of acetic acid aqueous solutions<sup>82</sup>.

Among the above-mentioned acids, HLac and H<sub>2</sub>Suc demonstrated the highest efficiency in Co-leaching in water. A larger scale experiment performed with an HLac aqueous solution (1 M, 7 L, L/S=14 for limiting the amount of solution) on 650 g of WC-(20 wt.%)Co powder under forced aeration conditions, showed a 79 wt.% of Co dissolution occurred in 24 h. C and O content in the treated WC-Co powders was found to be higher than the optimal rate expected for sintering a good quality HM (see Table 5,<sup>83</sup>). Thermal treatments under an inert environment (1000 °C, 2 h, N<sub>2</sub>) were, hence,

necessary and able to drive powder composition within the desired ranges suitable for HM production.

Table 5 - Desired and found C and O percentage composition for WC-Co recovered powders before and after thermal treatment<sup>83</sup>.

	<b>C (%)</b>	<b>O (%)</b>
Optimal WC-Co powder	5.70	≤0.40
HLat <sub>(aq)</sub> /O <sub>2</sub> -WC-Co	6.24	1.60
HLat <sub>(aq)</sub> /O <sub>2</sub> -WC-Co after heating	5.65	0.19

As demonstrated in the previously reported studies, the presence of oxidants enhances the dissolution of Co in hydrometallurgical systems<sup>30</sup>. However, the use of water as the solvent and strong oxidizing agents (O<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>) generate oxidation/hydration phenomena on the recovered WC particle surface<sup>84</sup>.

To prevent these undesired phenomena which heavily affect the number of stages necessary for efficient secondary material recovery, an alternative leaching approach may be represented by solvo-metallurgy. An example of a highly selective solvo-metallurgical leaching with organic acids has been recently proposed, using alcohols instead of water as the reaction media to recover internal powder scraps generated during the HM manufacturing process<sup>84</sup>. Specifically, the behaviour of different citric, lactic and maleic acid solutions in ethanol was investigated without additional oxidizing agents. Preliminary tests were carried out on Co metal powder with different leaching conditions to identify the most promising to apply on real waste samples. The importance of the presence of a low amount of water in the solvent for the Co complex formation was also investigated. 0.1-0.5 M maleic acid solutions in ethanol 96 vol.% demonstrated to dissolve almost quantitatively Co-powder within 4 h at room temperature and pressure. Differently, citric and lactic acid solutions achieved a complete Co dissolution within around 12 and 38 h, respectively, at 1 M concentration. This finding agrees with the increasing weakness of the acids in the order maleic < citric < lactic (pK<sub>a1</sub> in water at 25°C

= 1.76, 2.90 and 3.67, respectively)<sup>85</sup>, even more significant in ethanol concerning water, and with the decreasing evidence of H<sub>2</sub> gas evolution during the reaction along the series (inappreciable in the case of lactic acid solutions). Due to its high efficiency still at very mild conditions with no need of external oxidants and giving a reaction where no precipitations occur, 0.5 M maleic acid solution in ethanol with L/S=14 L/kg, were applied to two WC-Co powder samples with approximately the same Co content (20 wt.%) but different WC grain size in the sintered specimen. Small-scale tests (0.5 g of WC-Co powder) pointed out a better leaching efficiency on the sample with coarser WC grains, probably due to the higher values of Co mean free path, reaching a complete Co removal in 3 h. A larger scale experiment (300 g of WC-Co powder) was then performed to verify that the treated powder met the industrial requirements to be directly re-employed in HM manufacturing. Results of the Metallurgical Quality Control (MQC) on bars obtained by sintering the recovered powder after leaching, compared with the same values related to the use of the pristine powder as well as with reference values for an HM with a composition close to one of the treated sample, demonstrated the good quality of the recycled material.

The importance of these preliminary results lies in the promising application of organic acids and solvo-metallurgy in metals valorisation from HM manufacturing, increasing selectivity and reducing the number of metallurgical treatments for recovery. On the other side, it is worthy to note that the use of volatile organic compounds (VOCs) as leaching media in place of water may add safety concerns for their flammability and requires recycling to limit the costs.

### **4.3 Bio-based organic acid leaching of oxidized WC-Co**

Oxidative processes on WC-Co-based scraps make them brittle to be pulverized easily and to remove oils and solvents in sludge. During these processes, WC and Co are converted to WO<sub>3</sub>, CoWO<sub>4</sub>, and, rarely, Co-oxides with the result that the Co becomes less reactive and more resistant to the chemical leaching while W, here present as W(VI), more prone to leaching and complexation. From a chemical point of view, in these systems the role of organic acids becomes crucial, due to the higher pH they

confer to their solutions concerning inorganic acids, as well as for the complexing properties their deprotonated forms show with metal species, including W(VI). This statement finds support on the experimental evidence collected by a number of different authors working on the base chemistry of W since early '900.

Specifically, it is well known that W(VI) forms a number of different polynuclear species with different solubility in water<sup>86-89</sup>, dominated by:

- $\text{WO}_4^{2-}$  ion at  $\text{pH} > 7.8$ ;  $\text{W}_{12}\text{O}_{42}^{12-}$  at  $\text{pH} < 7.8$ ;  $\text{W}_{12}\text{O}_{42}^{12-}$  protonate forms at  $\text{pH} < 5.7$ <sup>87</sup>
- $\text{W}_{12}\text{O}_{41}^{10-}$  and  $\text{HW}_6\text{O}_{21}^{5-}$  at  $\text{pH} = 5$ ;  $\text{H}_3\text{W}_6\text{O}_{21}^{3-}$  at  $\text{pH} = 4$ , which with time forms the stable meta-tungstate ion  $[\text{H}_2(\text{W}_3\text{O}_{10})_4]^{6-}$ <sup>89</sup>
- low-solubility  $\text{WO}_3 \cdot 2\text{H}_2\text{O}$  at  $\text{pH} = 1$ <sup>90</sup>.

Furthermore, numerous organic compounds containing -COOH and -OH groups, are known to work as good complexing agents for W(VI)<sup>91</sup>.

In 1992, De Carvalho et al. reported a systematic study addressed to compare the influence of the presence of W(VI) (or Ca(II)) complexing agents on the dissolution of scheelite ( $\text{CaWO}_4$ ) either in alkaline ( $\text{Na}_2\text{CO}_3$ ) or acid (HCl) solutions. Monocarboxylic acids (formic and acetic), dicarboxylic acids (oxalic<sup>92,93</sup>, malonic and fumaric<sup>93</sup>), hydroxycarboxylic acids (lactic<sup>94,95</sup>, malic<sup>96</sup>, tartaric<sup>94,97</sup> and citric<sup>94,98</sup>), benzenocarboxylic acids (salicylic, gallic and pyrogallic<sup>99</sup>), were selected and investigated besides aldoses and sugar acids (galactose<sup>100</sup>, sorbitol<sup>101,102</sup> and gluconic acid<sup>94,103</sup>) as well as guanidine chloride<sup>104</sup>, humic acid and EDTA<sup>105,106</sup>. Alkaline solutions seemed in general preferable for tungsten dissolution because of the higher solubility of W(VI)-based compounds, which was also increased by the formation of high stability complexes with appropriate complexing agents such as EDTA, galactose, tartaric, salicylic, gallic and humic acids. Instead, in an acid medium, all the complexing agents used gave substantially higher leaching values than when no complexing agent is present, with the best results obtained with oxalic, tartaric, malic, lactic, citric and gluconic acids, which extract 90-100% of tungsten present between 1 and 50 days<sup>91</sup>.

Table 6 summarizes the results obtained by treating oxidized WC-Co-based scraps with organic acids and the corresponding process conditions as described by the work of Seo and Kim. Specifically, they investigated Co dissolution from oxidized WC-Co scraps with malic acid solutions with varying process parameters, such as solution concentration and temperature, stirring rate and mode, as well as H<sub>2</sub>O<sub>2</sub> addition. The WC-9 wt.%Co scraps selected for this study, consisting of rejected cutting tools, underwent thermal treatment at 900 °C for 3 h in an oxygen atmosphere to obtain WO<sub>3</sub> and CoWO<sub>4</sub>. Leaching experiments carried out on the grounded material highlighted that 1-3 M malic acid aqueous solutions, in the presence of 2 vol. % H<sub>2</sub>O<sub>2</sub>, can dissolve up to 50 wt.% of CoWO<sub>4</sub> at 20 °C and magnetic bar stirring (200 rpm) within 144 h. Passivation phenomena related to the formation of an insoluble tungstic acid layer on the CoWO<sub>4</sub> surface were suggested by authors as the main factor which hampers the leaching efficiency. On the other side, H<sub>2</sub>O<sub>2</sub> addition seemed to slightly increase efficiency reasonably through the conversion of tungstic acid into the more soluble peroxotungstic acid<sup>41,107</sup>.

A comparison of the previously described results was made by the same authors with a wet milling system where grinding and leaching go on simultaneously into rotating jars loaded with ZrO<sub>2</sub> balls (see Figure 7).

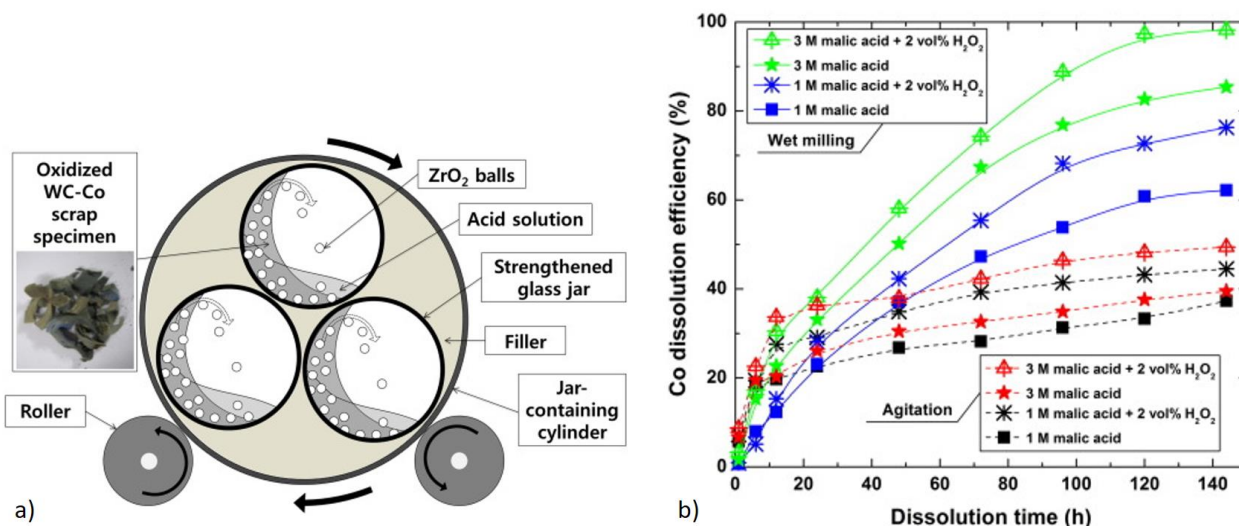


Figure 7 - a) Schematic diagram of a ball mill used in wet milling process. It shows main components of wet milling for Co dissolution from oxidized WC-Co scrap fragments (optical image); b) comparison among leaching profiles of CoWO<sub>4</sub> with malic acid solutions by stirring (below) and wet milling (above)<sup>41</sup>.

In these conditions, Co dissolution with 1-3 M malic acid solutions and 2 vol.% H<sub>2</sub>O<sub>2</sub>, at 20 °C, reached up to 98.2% yield within 144 h, with respect to about 50% obtained by simple agitation on the grounded material. The adoption of a ball milling activation makes the use of diluted solutions of malic acid a valued alternative to strong inorganic acids like sulphuric acid (almost quantitative CoWO<sub>4</sub> dissolution in similar experimental conditions, see sect. 2.2). Malic acid solutions were demonstrated to be the most effective in leaching, concerning sulphuric acid and citric acid, when no H<sub>2</sub>O<sub>2</sub> is added to the reaction (CoWO<sub>4</sub> dissolutions yield in 24 h: 25% with malic, 8% sulphuric, 13% citric acids at 1 M concentration), attributed by the authors to its better coordinative properties towards Co ( $pK_{\text{form}} [\text{CoHMa}] 4.31 > pK_{\text{form}} [\text{CoH}_2\text{Cit}]^+ 1.25$ ). Noteworthy, a satisfactory 85% CoWO<sub>4</sub> leaching (*vs* almost quantitative in the presence of H<sub>2</sub>O<sub>2</sub>) was found by wet milling of oxidized scraps with a 3 M malic acid solution at 20 °C within 6 days. On the other side, as mentioned before, the use of zirconia balls has to be carefully evaluated due to possible contamination effects of the final product.

Furthermore, referring to the known and cited reactivity of carboxylic organic acids towards W(VI) and the species it forms at  $\text{pH} > 1$ , besides the observed  $\text{CoWO}_4$  dissolution, the leaching of  $\text{WO}_3$ -based compounds may also be expected in an acid environment, even if no specific attention in the reported papers has been devoted to. For this reason, a strict comparison between weak-complexing and strong inorganic acid efficiency at the same concentration conditions does not seem appropriate due to the different roles played by the  $\text{H}^+$  and anions species in the leaching reaction pathways. Specifically, a relevant consumption of the leaching agent for W complexation should be carefully taken into account when the cited class of organic acid is used towards oxidized HM scraps, because they can affect  $\text{CoWO}_4$  leaching efficiency and selectivity.

These aspects suggest focusing on the industrial requirements for applicative purposes for defining the most appropriate leaching system and conditions. In that sense, the lower pH and less effective complexing action provided by, coupled with the good efficiency in  $\text{CoWO}_4$  dissolution in the presence of  $\text{H}_2\text{O}_2$ , make strong inorganic acids the preferred lixiviants when a high selectivity is requested for secondary materials application. Differently, organic acids solutions allow combining mild leaching conditions and reactants with significant effectiveness in Co- and W-oxidized species, opening the way to a wide spectrum of applications for the recovered products, as observed for alkaline-based chemical recycling treatments. In that sense, as schematized in Figure 5, the use of organic acid solutions may represent a promising alternative to the use of strong inorganic bases, widely increasing the versatility of acid leaching in metals recovery from HM waste.



Table 6 – Organic acid leaching treatments on oxidized WC-Co scraps as reported by Seo and Kim<sup>41</sup>.

Acid	Specimen characterization	Thermal Oxidation [°C] and pre-treatments	Operational conditions						Optimal conditions	Results	Comments
			Concentration [M]	Powder/Liquid [g/L]	Temperature [°C]	Added Oxidant	Reaction time [h]	Stirring [rpm]			
Citric	9% Co in WC-Co scrap	900 °C for 3h ball milling up to $\phi = 2-3 \mu\text{m}$	1	50	20	H <sub>2</sub> O <sub>2</sub> (2% vol)	24	200	1 M, 20 °C, H <sub>2</sub> O <sub>2</sub> , 24 h, 200 rpm	15% of Co leaching	
Malic	9% Co in WC-Co scrap	900 °C for 3h ball milling up to $\phi = 2-3 \mu\text{m}$	0.1-3	50	20-70	H <sub>2</sub> O <sub>2</sub> (2% vol)	6-72	200	1) 1 M, 70 °C, 72 h, 200 rpm 2) 1 M, H <sub>2</sub> O <sub>2</sub> (2% vol), 72 h, 20 °C, 200 rpm	28.2-53% of Co leaching	Co dissolution rate increases in hot malic acid (1) and adding H <sub>2</sub> O <sub>2</sub> (2)
		900 °C for 3h	1-3	50	20	H <sub>2</sub> O <sub>2</sub> (2% vol)	144	-	3 M, H <sub>2</sub> O <sub>2</sub> (2% vol), 20 °C, 150 g ZrO <sub>2</sub> balls	Almost complete Co leaching	Simultaneous milling and Co dissolution; the use of zirconia balls may cause contamination

## 4.4 Cobalt recovery from leaching organic acid solutions

Following the leaching phase, that is one of the most critical aspects on the whole recovery process, the enhancement of Co in a form suitable for application is a further issue of industrial interest. Besides the possible applications of the complex as it is<sup>108</sup>, directly crystallized by the leaching solution, a series of separation & recovery processes for achieving Co derivatives of industrial interest may be approached.

Three main classes of processes are typically applied:

- the thermal degradation of the leaching compounds to form Co metal or Co-oxides;
- the selective precipitation of a low-solubility Co-derivatives of industrial interest (e.g.  $\text{Co}(\text{OH})_2$ ,  $\text{CoCO}_3$ ,  $\text{CoC}_2\text{O}_4$ , etc.);
- the electrodeposition of Co metal from the leaching solution.

Among the three, the thermal treatment is able to recover Co in high yield, but the process is energy demanding as well as it does not prevent lixiviant degradation and  $\text{CO}_2$  emissions. Examples of pyrolysis at high efficiency were provided by Gurmen, using an ultrasonic spray pyrolysis on nitric acid leaching solution to obtain nano-sized pure cobalt metal powder<sup>84</sup>.

Differently, the selective precipitation as well as the electrowinning of the leaching solution may achieve purer Co-containing products/metal and the recovery of the leaching agent as well as of the used solvent, limiting wastewater production.

As an example, ref. <sup>84</sup> describes a twofold approach for Co recovery from  $[\text{Co}(\text{HMal})_2(\text{H}_2\text{O})_4]$  solutions. Specifically, as summarized in Figure 8, Co metal was recovered by electrowinning of a  $[\text{Co}(\text{HMal})_2(\text{H}_2\text{O})_4]$  aqueous solution, using copper spiral cathodic and platinized titanium anodic electrodes, under constant current of 36 mA (resulting in a constant DC density of 12 mA/cm<sup>2</sup> 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. On the other side, a selective almost quantitative precipitation of  $\text{CoCO}_3$  was obtained by adding  $\text{Na}_2\text{CO}_3(\text{aq})$  to  $[\text{Co}(\text{HMal})_2(\text{H}_2\text{O})_4](\text{aq})$ , allowing the recovery of  $\text{H}_2\text{Mal}$ .

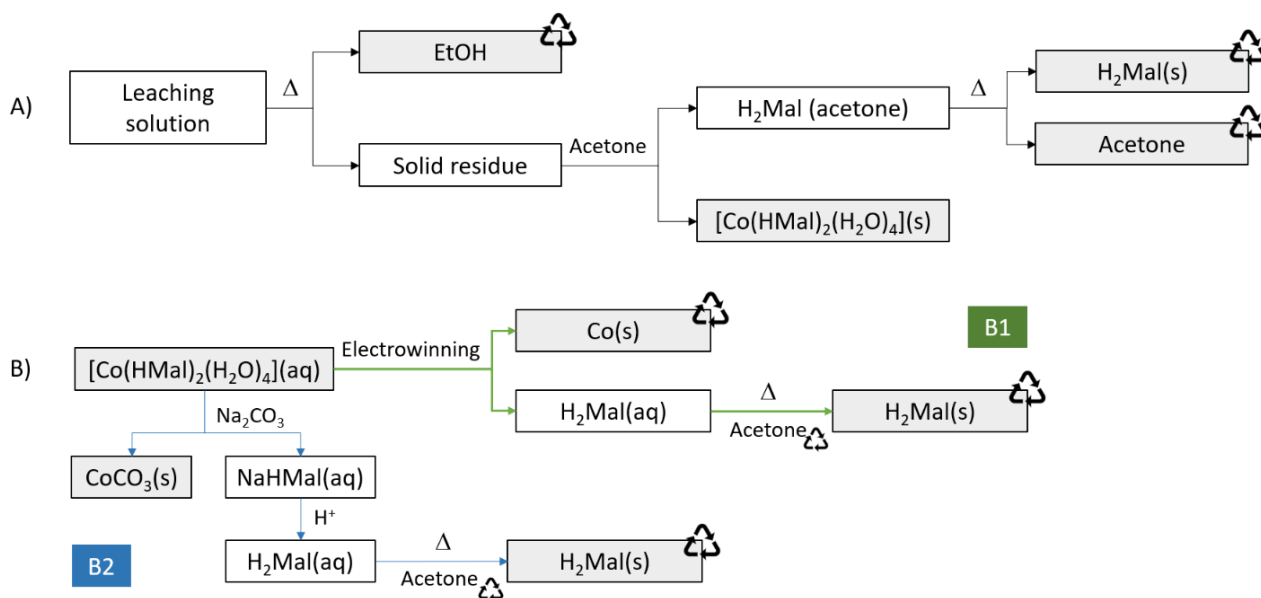


Figure 8 - Schematic diagram for cobalt, reagent and solvent recovery from the leaching solution as reported in ref. <sup>84</sup>. Phase A): recycling of ethanol and unreacted  $\text{H}_2\text{Mal}$ , isolation of  $[\text{Co}(\text{HMal})_2(\text{H}_2\text{O})_4](\text{s})$ ; Phase B): alternatively, electrowinning (B1) or Co-precipitation in a commercially viable form (B2).

Edtmaier et al., also suggested the selective precipitation of  $\text{Co}_3\text{O}_4$  from a cobalt acetate solution and the recovery of acetic acid, which in turn can be used for a new run of the dissolution process<sup>82</sup>.

The non-harmful nature of organic acids coupled with their easy recyclability in the same recovery process, make these acids particularly appealing for this kind of application.

## 4 Conclusions

HMs play a fundamental role in many industrial processes and their importance is growing over time, because they fulfil the requirements of many innovative application sectors. Over the past decade, the criticality of the main raw materials for HM manufacturing have increased dramatically. Conse-

quently, the valorisation of HM waste and production by-products is of paramount importance especially as it expands with the growth of the global population. Therefore, what was a good practice in the HM sector to recycle part of the waste, must now be recognized as a primary objective, in order to safeguard natural resources, critical metals and prevent the disposal of toxic metals. Furthermore, this must be seen in the perspective of having more sustainable production and recycling processes. In this context a key role is played by hydrometallurgy, as an alternative or a complement of widely used thermal treatments. In this review, the peculiar behaviour of not harmful bio-based organic acids in assisting hydro- or solvo-metallurgy is critically approached with the view of opening a discussion on the potential use of these gentle but powerful lixivants in HM manufacturing. More specifically, despite the early-stage of the research in this field, results reported in the literature suggest a crucial contribution of weak organic acids in:

- semi-direct acid leaching on WC-Co-based soft scraps, both by hydro- and solvo-metallurgy, where the complexing properties of the deprotonated acids enhance selectivity and efficiency, limiting or avoiding the use of additional oxidizing agents;
- treating oxidized HM scraps in order to recover metals at the highest rate and versatile form possible, in order to provide a suitable tool for W- and Co-based chemicals production, nowadays achievable only by alkaline chemical recycling.

A further relevant contribution has been demonstrated in improving efficiency of electro-dissolution processes, opening the way to deeper investigations on new electro-leaching systems based on organic acid solutions working in water and/or in non-water solvents.

The use of organic acids, in particular the bio-derived ones, facilitates the transition towards as green as possible economy models through an industrial biorefinery implementation. This model establishes

a bridge between different industrial worlds (the agro-industrial one, from which many of the substrates used come, and the manufacturing one) thus expanding the radius of circularity of resources, in accordance with the circular economy principles set in the EU action plan<sup>109</sup>.

Despite at this stage the exact amount of OA needed to treat a unit of HM scrap is not known, based on the annual HM production (estimated between 50 and 100 kt worldwide) and the current production capacity of OAs (e.g. around 20 Mt of acetic acid and 2 Mt lactic acid produced each year worldwide by renewable sources), it seems OA availability may largely cover the request for HM recycling. In this framework, the valorisation of non-food agro-industrial residues for producing bio-derived chemicals is collecting increasing attention, on the one hand, to increase the production capacity of organic acids, and, on the other hand, to obtain low-cost valued products, limiting waste/wastewater disposal as well as the chemical conversion of precursors from petroleum processes. Among these, pioneering hydro- and solvo-metallurgical applications of organic acid-based solutions obtained by agro-industrial waste, have been recently proposed<sup>110,111</sup> and stimulate further research efforts for meeting technical-economic-environmental sustainability requirements.

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