

# A comparison among bio-derived acids as selective eco-friendly leaching agents for cobalt: the case study of *hard metals* waste enhancement

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## Abstract

Peculiar chemical, mechanical and magnetic properties make cobalt a key metal for a variety of “hot” applications like cathode production of Li-ion batteries. Cobalt is also the preferred metallic binder for tungsten carbide tools manufacturing. The recent increasing criticality of cobalt and tungsten is driving the interest of manufacturers and researchers towards high-rate recycling of Hard Metals (HMs) waste for limiting the demand of raw materials. A simple and environmentally friendly hydrometallurgical route for Co selective dissolution from HM wastes was developed by using weak, bio-derived and biodegradable organic acids (OAs). In this study OAs, namely acetic (HAc), citric (H<sub>3</sub>Cit), maleic (H<sub>2</sub>Mal), lactic (HLac), succinic (H<sub>2</sub>Suc), lactobionic (HLB), and itaconic (H<sub>2</sub>It) acids, were selected for their pK<sub>a1</sub> values spanning from 1.8 to 4.7 and systematically tested as

selective cobalt leaching agents from WC-Co-based wastes in water, isolating the formed complexes at the solid state. Thereby, all of them seemed to be efficient in selective Co-leaching, achieving almost quantitative Co dissolution from HM by-products still at low concentration level and room conditions in a short time, leaving the residual WC unreacted and ready to be re-employed for industrial purposes. Nevertheless, two main categories of organic acids were distinguished depending on their oxidizing/complexing behavior: Class 1 OAs, where the metal oxidation is carried out by  $H^+$ ; Class 2 OAs where oxidation is played by an external oxidant like  $O_2$ . A combined experimental/theoretical investigation is here described to show the reasons behind this peculiar behavior and laid the foundation for a wider discussion on the leaching capabilities of OAs towards elemental metals. Due to the demonstrated effectiveness, low cost, eco-friendliness and large availability through biotechnological fermentative processes, particular attention is here devoted to the use of HLac in hydrometallurgy as an example of Class 2 OA. WC-Co materials recovered by HLac mild hydrometallurgy demonstrated a metallurgical quality suitable for re-employment in the HM manufacturing process.

## 1 Introduction

Cobalt is a metal with peculiar chemical, mechanical and magnetic properties which allow its use in numerous applications such as magnetic alloys,<sup>1</sup> catalysts,<sup>2</sup> batteries (especially Li-ion)<sup>3,4</sup> and other high-performance materials production.<sup>5,6</sup> Among the latter, cemented carbides, also referred to as hard metals (HM), 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, based on one or more elements from the iron group, i.e. Co, Ni, and Fe, with Co and its alloys the most widely used, acting as a matrix binder.<sup>7-9</sup> Thanks to their composite nature, HM exhibit an excellent combination of wear resistance and toughness, making them the natural choice for metal forming, cutting tools and wear parts since decades ago.<sup>5</sup> The wide and growing industrial use of cobalt and limited deposits worldwide, localized in a few countries, makes it a critical metal of strategic importance.<sup>7</sup> Specifically, in 2021 a 9.2 kt Co demand for hard-metal production (5.3% of global demand of Co) was recorded, of which around 60% was supplied by the Democratic Republic of Congo (DRC).<sup>10,11</sup> On account of this aforementioned scarcity and the socio-political concerns related to the most relevant cobalt supplying countries, methods addressed to limit the use of natural reserves by recovering it from secondary raw materials like waste are stimulated and in line with worldwide directives addressed to circular economy models.<sup>12,13</sup>

Currently, a variety of methods for the enhancement of cobalt-containing waste generally exploit the use of dangerous reagents (primarily strong oxidizing acids) and / or aggressive operating conditions (high temperatures).<sup>14,15</sup> In the last decade, the use of bio-derived organic acids (OAs) as leaching agents is gaining increasing attention being safe, renewable and, in some cases, cheap substances. Thanks to their capability to dissolve low reduction potential metals, some of them have been recently proposed as suitable leaching agents for transition and rare earth<sup>1</sup> elements recovery from several kinds of waste. As an example, citric acid has proven to work as a powerful and *green* agent for Cu-based slags enhancement, removing effectively and selectively Co, Ni and Fe metal impurities from the composite material.<sup>16</sup> Similarly, citric and acetic acids were satisfactorily employed as effective leaching agents for NbFeB magnets - where also Co, Ni and several other REE in low amount are present - in mild conditions, achieving material dissolution in a short time.<sup>17</sup> Recently, we demonstrated the selectivity and efficacy of a new solvometallurgical Co-leaching method from HM

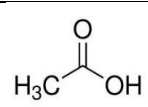
<sup>1</sup> Rare earth elements (REE), as defined by the International Union of Pure and Applied Chemistry, involve lanthanoides together with scandium and yttrium. Despite their name, their abundance in Earth's crust is relatively high.

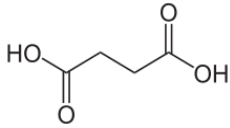
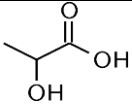
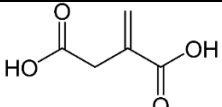
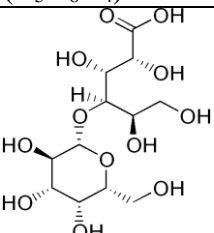
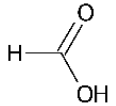
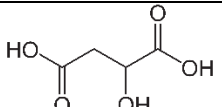
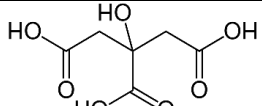
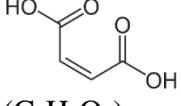
powders, based on the use of diluted maleic acid (H<sub>2</sub>Mal) ethanolic solutions working under gentle operative conditions.<sup>18</sup> Specifically, H<sub>2</sub>Mal (0.5 M, EtOH) selectively and quantitatively leached Co trapped within WC-Co powders, within 4 h at room temperature, leaving WC unreacted and ready for re-employment in HM manufacturing.

In these processes, the organic acid can work as complexing and oxidizing – by H<sup>+</sup> – agent towards elemental state metals. More specifically, it will be able to couple complexing and oxidizing actions when its pK<sub>a</sub> and/or the K<sub>diss</sub> of the formed complex are very low. Differently, the role played by the acid is mainly related to the complexing properties of its deprotonated (anionic) form, thus an external oxidizing agent is necessary for the metal(0) leaching, as observed in the case of the use of acetic acid solutions (pK<sub>a</sub> = 4.7) towards WC-Co wastes which requires forced O<sub>2</sub> addition to the leaching system for driving the Co-dissolution reaction.<sup>19</sup> Other examples are related to the use of OAs for metal leaching from oxidized materials. Due to the amount of waste we will soon have to deal with, the case attracting the most attention recently is the application of OAs like acetic, ascorbic, citric, lactic, maleic, malic and succinic, in the presence of H<sub>2</sub>O<sub>2</sub>, for lithium and cobalt recovery from spent Li-ion batteries (LIBs).<sup>4,20</sup> Besides, several examples for Co recovery from oxidized HM scraps were also proposed, as in the case of the use of malic acid/H<sub>2</sub>O<sub>2</sub> for Co leaching from CoWO<sub>4</sub>.<sup>21</sup> In these cases, the role of the organic acid is mainly related to its coordinative behavior towards the metal ion and the formation of metal complexes soluble in the leaching solvent. In some cases, a lower effectiveness in leaching reactions carried out by weak organic acids vs. strong inorganic acids, is observed. Against, the use of weak coordinating acids may increase selectivity, limits by-products formation and makes safer the process for operators and the environment. Noteworthy, a good exposure of metal values to the chemical etching results in good improvements in the leaching rate.

On this basis, the present paper introduces a fundamental study of the reactions between several selected bio-derived organic acids and cobalt metal in water. OAs were selected among complexing carboxylic acids, based on their easy availability, renewability, and eco-friendliness, taking into account their acidity in water, as summarized in Table 1. The systematic approach allowed to highlight, through experimental evidences as well as calculations, how the complexing capability of the leaching agent together with its K<sub>a1</sub> may affect the reduction potential of both the metal and the proton. The role of the acid in the reaction, the most appropriate leaching conditions and the obtained complexes are here systematically investigated, allowing the suitability of the different acids for HM waste enhancement applications to be assessed. Then, the manuscript describes a full process of material recovery from WC-Co waste powders by using diluted HLaq aqueous solutions, identified as the most promising for practical applications, due to its low cost, high efficiency towards both Co powder and Co contained as a binder in the real WC-Co powders and large availability through organic substrates fermentation.

**Table 1.** Organic acids used in this work, listed by decreasing pK<sub>a1</sub> values. MM = molar mass.

Name (acronym used herein)	Formula	pK <sub>a1</sub> (25°)	Current bio-production
Acetic Acid, Ethanoic acid (HAc)	 (C <sub>2</sub> H <sub>4</sub> O <sub>2</sub> )	4.56 <sup>22</sup>	Acetogenesis, acetic fermentation and yeast fermentation

Succinic acid, 1,4- butanedioic acid <b>(H<sub>2</sub>Suc)</b>	 (C <sub>4</sub> H <sub>6</sub> O <sub>4</sub> )	3.99 <sup>22</sup>	Bio-production from different carbon sources (galactose, galactose/glucose, and galactose/lactose)
Lactic acid, 2-hydroxypropanoic acid <b>(HLat)</b>	 (C <sub>3</sub> H <sub>6</sub> O <sub>3</sub> )	3.67 <sup>22</sup>	Fermentation of sugars, mainly glucose and sucrose
Itaconic acid, 1-Propene-2,3- dicarboxylic acid <b>(H<sub>2</sub>It)</b>	 (C <sub>5</sub> H <sub>6</sub> O <sub>4</sub> )	3.66 <sup>22</sup>	Fermentation of lignocellulosic biomass or with metabolically engineered bacteria
Lactobionic acid, 4-O-beta- galactopyranosyl-D- gluconic acid <b>(HLB)</b>	 (C <sub>12</sub> H <sub>22</sub> O <sub>12</sub> )	3.6 <sup>23</sup>	Bio-production from whey or through the biological oxidation of lactose
Formic acid, methanoic acid <b>(HFor)</b>	 (CH <sub>2</sub> O <sub>2</sub> )	3.57 <sup>22</sup>	Bio-production from cellulosic biomass
Malic acid, 2- Hydroxybutanedioic acid <b>(H<sub>2</sub>Ma)</b>	 (C <sub>4</sub> H <sub>6</sub> O <sub>5</sub> )	3.24 <sup>22</sup>	Microbial fermentation from renewable raw materials such as lignocellulose
Citric acid, 2-hydroxy-1,2,3- propane tricarboxylic acid <b>(H<sub>3</sub>Cit)</b>	 (C <sub>6</sub> H <sub>8</sub> O <sub>7</sub> )	2.90 <sup>22</sup>	Fermentation of glucose or sucrose through bacteria, fungi and yeasts
Maleic acid, <i>cis</i> -Butenedioic acid <b>(H<sub>2</sub>Mal)</b>	 (C <sub>4</sub> H <sub>4</sub> O <sub>4</sub> )	1.76 <sup>22</sup>	Synthesized by fungi such from renewable substrates or through sustainable biomass-based feedstocks catalytic conversion

## 2 Materials and Methods

All chemicals were used as purchased without any purification (Sigma-Aldrich: Succinic acid, 99%. TCI: Maleic acid, >99.0%. Carlo Erba: Citric acid monohydrate RPE; Acetic acid glacial RPE. Acros Organics: Itaconic acid, 99+%; Lactobionic acid, 97%. ACEF: Lactic acid FU-BP E 270). Cobalt powder was used as purchased by Umicore (Extrafine, >99.5 wt%, 1.3 μm). WC-Co powders (RC-627C and RC-631L), were provided by F.I.L.M.S. SpA, Anzola D'Ossola, VB (IT).

### 2.1 Test specimen definition

WC-Co powders studied throughout this work, namely RC-627C and RC-631L, are by-products of HM manufacturing, generated during machining operations by F.I.L.M.S. SpA. The Co content of the binder phase in the test specimen is 19.6 and 20.4 wt. %, respectively (full composition is provided in Supplementary Material). The morphology and WC particle size of these powdered samples were determined using Scanning Electronic Microscopy (SEM) whilst optical microscopy (OM) was used to characterize the corresponding sintered samples.

## **2.2 Leaching procedures**

### **2.2.1 Co-powder**

Co metal powders (0.020 g, 0.34 mmol) were reacted with 0.050L of a 0.5M aqueous leaching solution of the selected acids in an open flask under room conditions (approximately 20°C and 1 atm) and magnetic bar stirring (300 rpm). The solutions turned readily from colorless to bright pink and the disappearance of Co powder occurred in a short time. The obtained cobalt complexes were isolated in the solid state from the leaching solution through the diffusion of acetone in the aqueous solution. The dried solids were subsequently characterized as in Sects. S1.2 and S1.3. Similar experiments using Co powder (0.160 g) and OA(aq) (0.5 M, 400 mL) were run into capped 1 L plastic bottles in attrition mode (Heidolph REAX 20 rotating system, 5 rpm) with the view to highlight gas formation/consumption during the leaching process through a corresponding volume expansion/shrink of the container.

### **2.2.2 WC-Co test specimen**

Co-leaching experiments on test specimens were carried out by reacting 500 mg of sample with an aqueous solution of each of the respective acids (250 mL, 0.5M) in an open flask at room temperature under magnetic bar stirring (300 rpm). In each case, the leaching process was monitored over 1-12 hours by 1 h increments. Co-recovery yields were determined incrementally based on the elemental analysis (ICP-OES) of the leachate aliquots after digestion (see Sect. S1.1).

### **2.2.3 Scale-up process**

A 650 g aliquot of RC-631L was reacted with HLac(aq) (1 M, 7 L, L/S = 14 L/kg) at room temperature (20 °C) and pressure in the presence of forced aeration in a 30 L mixing vessel. Stirring was provided by bubbling air from the bottom of the vessel through spherical porous stones connected to an air compressor. The leaching reaction was monitored from 1 to 24 hours by sampling the leachate and analyzing for Co the digested aliquots by ICP-OES.

### **2.2.4 Process demand of oxygen (respirometry)**

The respirometer is a system typically used for the measurement of the biochemical oxygen demand (BOD) in water, or the amount of oxygen that is consumed during the decomposition of organic matter in soils or composts. The system (Sapromat apparatus, H+P Labortechnik AG, Germany) consists of a 500 mL glass reaction bottle containing the sample, connected to a sensor and an O<sub>2</sub>-generator. At the time when there is a net oxygen consumption (i.e. in the absence of any other gas production due to the specific reaction involved), an electrode system detects the depression in the glass reaction bottle and supplies a parceled amount of oxygen. Flasks are placed in a thermostated bath at 20°C under magnetic bar stirring.

## **3 Results and discussions**

### **3.1 Leaching experiments on Co powder**

With the view to investigate the chemical reaction occurring between the selected lixivants and cobalt in water, Co metal powders were reacted with an excess of diluted aqueous leaching solutions of the selected acids in an open flask under room conditions as detailed in Sect. 2.2.1. Effective reactions took place in all cases under study, providing bright pink colored solutions and the full disappearance of Co powder occurred in short times (3-12 h). The leaching reactions occur by concerted oxidation and complexation of the metal forming, in a single-stage, the corresponding Co-complex which was isolated, in most cases, at the solid state by concentration and selective precipitation. The recovered compounds were, hence, characterized as detailed in Supplementary Material, Sect. S1, and the most of them recognized as already well-known, even if typically reported in the literature as the products of complexing reactions.

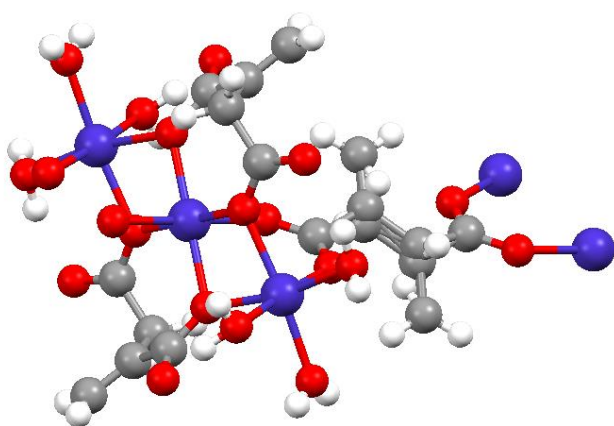
Table 2 summarizes the Co-leaching reactions occurring with the different acids in water and the corresponding primary products (Sects. S1.2 and S1.3 for characterization).

**Table 2.** Leaching reactions occurring with the different acids in water. \*Main known product in water.

Organic acid	Main leaching pathway found in water media	Leaching time (h)
HLac	$2\text{Co} + \text{O}_2 + 4\text{HLac} \rightarrow 2[\text{Co}(\text{Lac})_2(\text{H}_2\text{O})_2]$	4-5
H <sub>2</sub> Suc	$\text{Co} + \text{H}_2\text{Suc} + n\text{H}_2\text{O} \rightarrow [\text{Co}(\text{Suc})(\text{H}_2\text{O})_n] + \text{H}_2$ $2\text{Co} + \text{O}_2 + 2\text{H}_2\text{Suc} + (n-2)\text{H}_2\text{O} \rightarrow 2[\text{Co}(\text{Suc})(\text{H}_2\text{O})_n]$	4-5
H <sub>2</sub> It	$3\text{Co} + \text{H}_2\text{It} + 3n\text{H}_2\text{O} \rightarrow [\text{Co}(\text{It})(\text{H}_2\text{O})_n]_3 + \text{H}_2$ $6\text{Co} + 3\text{O}_2 + 6\text{H}_2\text{It} \rightarrow 2[\text{Co}(\text{It})(\text{H}_2\text{O})_n]_3 + (6-3n)\text{H}_2\text{O}$	4-5
HLB	$2\text{Co} + \text{O}_2 + 4\text{HLB} \rightarrow 2[\text{Co}(\text{LB})_2(\text{H}_2\text{O})_2]$	4-5
HAc	$2\text{Co} + \text{O}_2 + 4\text{HAc} + 4\text{H}_2\text{O} \rightarrow 2[\text{Co}(\text{Ac})_2(\text{H}_2\text{O})_4]^*$	4
H <sub>3</sub> Cit	$3\text{Co} + 2\text{H}_3\text{Cit} + n\text{H}_2\text{O} \rightarrow [\text{Co}_3(\text{Cit})_2(\text{H}_2\text{O})_n] + 3\text{H}_2$	11-12
H <sub>2</sub> Mal	$\text{Co} + 2\text{H}_2\text{Mal} + 4\text{H}_2\text{O} \rightarrow [\text{Co}(\text{HMal})_2(\text{H}_2\text{O})_4] + \text{H}_2$	3-4

Among the different compounds isolated by the listed reactions, well-shaped crystals for  $[\text{Co}(\text{It})(\text{H}_2\text{O})_2]_3$  suitable for X-ray measurements, gave the following described crystal structure.

Fig. 1 summarizes the crystal structure and parameters for  $[\text{Co}(\text{It})(\text{H}_2\text{O})_2]_3$  detailed in Sect. S2, similar to those described in ref. <sup>24</sup>.



Crystal system	orthorhombic
Space group	Pbca
a/Å	9.9809(13)
b/Å	14.5548(14)
c/Å	15.3513(19)
$\alpha$ /°	90
$\beta$ /°	90
$\gamma$ /°	90

**Figure 1.** Molecular structure and crystal parameters for  $[\text{Co}(\text{It})(\text{H}_2\text{O})_2]_3$  complex. Color legend: blue, Co; red, O; grey, C; white, H.

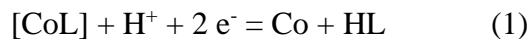
Even if an extensive description of the crystal structure of the products overcomes the scope of this work, it is worthy to note that all the compounds reported here are characterized bearing Co(II) in an octahedral environment, where the anionic form of the acid coordinates the metal center as monodentate or bidentate, chelating and/or bridging ligand and the coordination sphere is completed by water molecules according with the literature.<sup>25–28</sup> Specifically, the  $[\text{Co}(\text{IT})(\text{H}_2\text{O})_2]_3$  compound shows a peculiar trimeric structure where two  $\text{It}^{2-}$  anions behave as bidentate chelating ligands on the central Co atom and bridged with the two peripheral Co atoms. Further two  $\text{It}^{2-}$  anions act as monodentate on the central Co atom and behave as bridging ligands between two adjacent trimeric structures. The coordination sphere of the two peripheral Co atoms is completed by water molecules.

As summarized, leaching reactions, beside Co complexation, may involve the oxidizing action of the organic acid (through  $\text{H}^+$  reduction) which would result in  $\text{H}_2$  gas evolution and/or the oxidizing action of dissolved  $\text{O}_2$  which would be instead accompanied by  $\text{O}_2$  consumption and  $\text{H}_2\text{O}$  formation. Specifically, using maleic, citric, succinic and itaconic acids, the leaching was accompanied by a noticeable  $\text{H}_2$  gas evolution. Against, no gas formation was observed by leaching cobalt with lactic, lactobionic and acetic acid solutions. These results were supported by running the reactions into capped plastic bottles in attrition mode: where noticeable  $\text{H}_2$  evolution in an open flask under magnetic bar stirring was observed, a visible bottle expansion in the rotating closed system occurred; where there was no evidence of gas formation in the open flask, an evident gas consumption in the closed vessel (visible bottle shrink) occurred. Whereas, in the case of succinic and itaconic acid leaching, despite a noticeable gas evolution was present in the open flask reaction, no significant effects on the volume of the bottle when performed in the closed environment, were observed. This evidence suggested that, besides  $\text{H}_2$  production,  $\text{O}_2$  consumption may occur at comparable rates.

Despite the occurrence of these two possible pathways can be considered obvious, identifying the parameters able to drive the system to preferentially follow one specific pathway over the other may give relevant hints to designing appropriately the leaching system for applicative purposes.

As for a more formal description, a prediction of the spontaneity of the redox reaction between the metal and the  $\text{H}^+$  as oxidant has been made comparing the normal (apparent) reduction potential of the two species involved, taking into account the competitive complexation and acid dissociation equilibria occurring in water. With specific reference to Co leaching, as detailed in Supplementary

Material Sect. S3, we took into account that the ligands are involved in two different competing equilibria. Actually, the complex formation equilibria such as  $\text{Co} + \text{L} = [\text{CoL}]$  (L = organic acid in deprotonated form) operates simultaneously with the protonation equilibrium  $\text{H} + \text{L} = \text{HL}$ . To keep into account both processes in the interpretation of the redox behavior of  $\text{Co}^{2+}$ , we have therefore considered the following equilibrium:



The Nernst Equation for the redox potential of the reduction  $\text{Co}^{2+} + 2 \text{e}^- = \text{Co}$

$$E_{\text{Co}^{2+}/\text{Co}} = E_{\text{Co}^{2+}/\text{Co}}^0 + \frac{RT}{2F} \ln[\text{Co}^{2+}] = E_{\text{Co}^{2+}/\text{Co}}^0 + \frac{0.0592}{2} \log[\text{Co}^{2+}] \quad (2)$$

can be therefore rearranged to obtain the apparent reduction potential for the semi-reaction 1:

$$E_{\text{Co}^{2+}/\text{Co}}'' = E_{\text{Co}^{2+}/\text{Co}}^{0''} + \frac{0.0592}{2} \log \frac{[\text{CoL}][\text{H}^+]}{[\text{HL}]} \quad (3)$$

where

$$E_{\text{Co}^{2+}/\text{Co}}^{0''} = E_{\text{Co}^{2+}/\text{Co}}^0 - \frac{0.0592}{2} \log K_f + \frac{0.0592}{2} \text{p}K_a \quad (4)$$

The  $E_{\text{Co}^{2+}/\text{Co}}^{0''}$  differs from the expression of the typical  $E_{\text{Co}^{2+}/\text{Co}}^0$  (potentials corrected for the complex formation equilibria)<sup>29</sup> for a term dependent on  $\text{p}K_a$ . By evaluating the expression of  $E_{\text{Co}^{2+}/\text{Co}}^{0''}$  it is clear that its value decreases (metallic Co more oxidizable) with increasing stability of  $[\text{CoL}]$  species (higher  $K_f$ ) and with increasing strength of the acid (decreasing  $\text{p}K_a$ ). The relative magnitude of these two parameters for an organic acid under examination contribute to define the capacity of an organic ligand to form complexes with the cobaltous ion. This therefore justifies the use of  $E_{\text{Co}^{2+}/\text{Co}}^{0''}$  as a better parameter than  $E_{\text{Co}^{2+}/\text{Co}}^0$  to evaluate the redox behavior of cobalt in our conditions.

The calculations of the speciation of the  $\text{Co}^{2+}$ /ligand systems for the ligands examined (see Table 3) performed using the Hyss software<sup>30</sup> have shown that under the experimental conditions used in this work the proton dissociation is limited also for polyprotic ligands to the first ionization equilibrium. Also, the formation of complexes is limited to 1:1 metal:ligand species, even for acids that can form complexes with different stoichiometries (see Table S8 in Supplementary Material). These results justify the use of only  $\text{p}K_{a1}$  and  $\beta_1$  (hereafter  $\beta_1 = K_f$ ) as thermodynamic parameters.

As for the reduction potential of  $\text{H}^+$ , we took into account the protonation equilibria of the ligands, which led to the Nernst equation (see Supplementary Material, Sect. S3):

$$E'_{\text{H}^+/\text{H}_2} = E_{\text{H}^+/\text{H}_2}^{0'} + 0.0592 \log \frac{[\text{HL}]}{[\text{L}]} \quad (5)$$

where

$$E_{\text{H}^+/\text{H}_2}^{0'} = E_{\text{H}^+/\text{H}_2}^0 - 0.0592 \text{p}K_a \quad (6)$$

By evaluation of the expression of the two standard normal reduction potentials 4 and 6, it results that the process of oxidation of metallic cobalt by an organic acid pivots principally around the  $\text{p}K_a$  value.



Indeed, a low  $pK_a$  value results into a higher  $H^+$  concentration and in a lower HL concentration or possibly into the formation of [CoL] species, in turn making metallic cobalt more oxidizable.

The combination of the two semi-reactions leads to the following process:

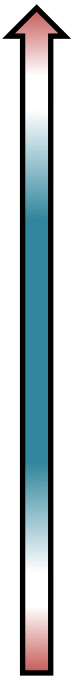


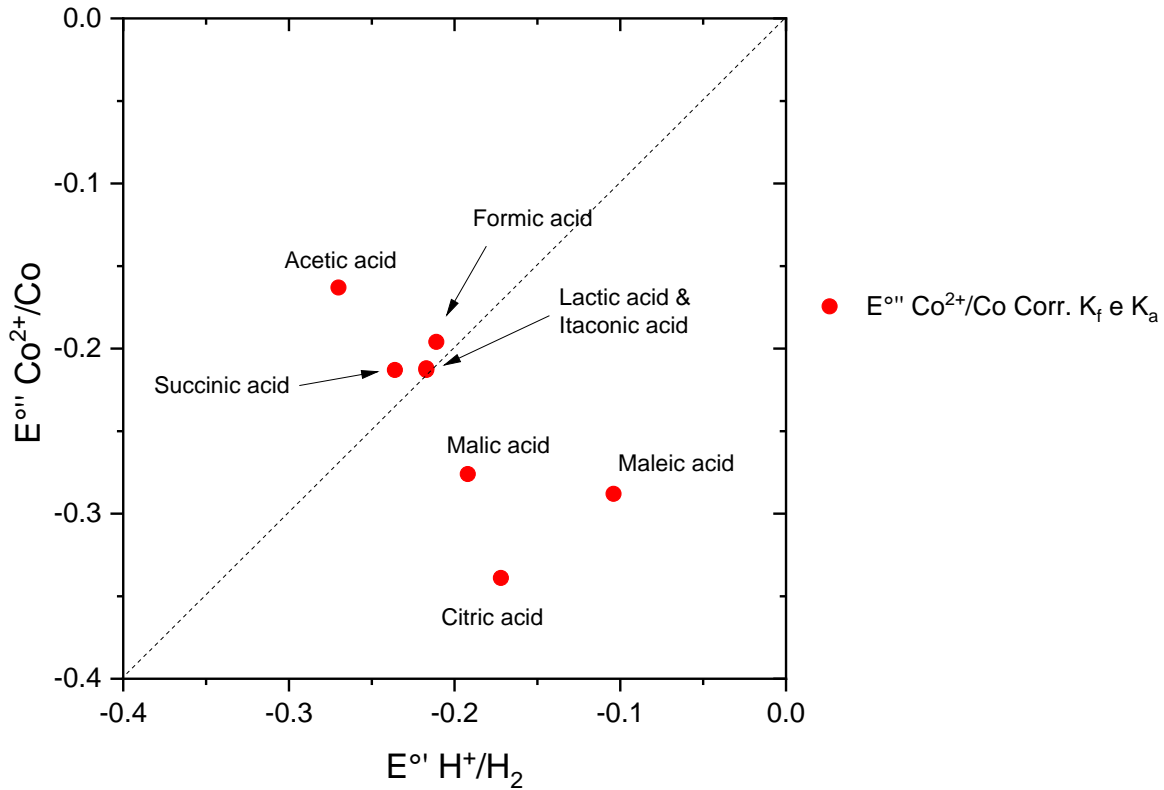
and to the related standard potential of the cell:

$$E_{cell}^{0'} = E_{H^+/H_2}^{0'} - E_{Co^{2+}/Co}^{0''} = E_{H^+/H_2}^0 - E_{Co^{2+}/Co}^0 + \frac{0.0592}{2} \log K_f + \frac{3 \times 0.0592}{2} \log K_a \quad (22)$$

Table 3 reports the  $E^{\circ\prime\prime}_{Co^{2+}/Co}$  and  $E^{\circ\prime}_{H^+/H_2}$  values calculated for the organic acids studied here, and the corresponding calculated  $E^{\circ\prime}_{cell}$ . The  $E^{\circ\prime\prime}_{Co^{2+}/Co}$  and  $E^{\circ\prime}_{H^+/H_2}$  values are also reported in graphic form in Figure 2. Those acids (points) that are in the bottom-right region of the plot have a significant tendency to oxidize metallic cobalt with formation of  $H_2$ , while those in the upper-left region are not prone to this process and the presence of a stronger oxidant such as dioxygen is required. Acids that are on or close the dotted line are those for which the process is not significantly favored on a thermodynamic basis, but it can occur if the actual concentrations of the components in the system allow it. Just as an example, in the presence of solely metallic cobalt the process may occur, and then rapidly stop because the redox cell potential reaches the value of zero.

**Table 3.**  $E^{\circ\prime}_{H^+/H_2}$ ,  $E^{\circ\prime\prime}_{Co^{2+}/Co}$  and  $E^{\circ\prime}_{cell}$  values. The  $pK_a$  values used are those reported at 25 °C.<sup>22</sup> As for the ionic strength, the values reported for  $I = 0.1$  M are used for homogeneity.

Spontaneity	ACID	$E_{H^+/H_2}^{0'}(V)$	$E_{Co^{2+}/Co}^{0''}(V)$	$E_{cell}^{0'}$	CLASS	Main oxidizing agent
	Maleic acid	-0.104	-0.288	<b>0.184</b>	<b>1</b>	<b>H<sup>+</sup></b>
	Citric acid	-0.172	-0.339	<b>0.167</b>		
	Malic acid	-0.192	-0.276	<b>0.084</b>		
	Lactic acid	-0.217	-0.213	<b>-0.005</b>	<b>2</b>	<b>O<sub>2</sub></b>
	Itaconic acid	-0.217	-0.212	<b>-0.005</b>		
	Formic acid	-0.211	-0.196	<b>-0.015</b>		
	Succinic acid	-0.236	-0.213	<b>-0.024</b>		
	Acetic acid	-0.270	-0.163	<b>-0.107</b>		



**Figure 2.** Plot of the  $E^{\circ}{}_{\text{H}^+/\text{H}_2}$ ,  $E^{\circ\prime\prime}{}_{\text{Co}^{2+}/\text{Co}}$  values calculated for the organic acids studied. Acids which refer to points in the bottom-right region are those expected to oxidize metallic cobalt.

Our calculations of the normal (or apparent) reduction potential under standard conditions  $E^{\circ\prime\prime}{}_{\text{Co}^{2+}/\text{Co}}$  opens a window on the rationalization of the relative occurrence of the observed redox reactions. As pointed out, their occurrence is related to the relative reduction potential of the interacting species ( $E_{\text{Co}^{2+}/\text{Co}}$  vs  $E_{\text{H}^+/\text{H}_2}$  and  $E_{\text{O}_2/\text{H}_2\text{O}}$ ) as well as the relative concentration of the oxidizing species in solution. Indeed, on the one hand, the stability of the formed metal complex lower the reduction potential of the metal making it easier to be oxidized as well as the reduction potential of the  $\text{H}^+/\text{H}_2$  couple, when weak acids (high  $\text{p}K_{\text{a}1}$  values) are involved. On the other hand, despite the higher reduction potential of  $\text{O}_2$  with respect to  $\text{H}^+$ , the low solubility and diffusion rate of gaseous  $\text{O}_2$  in water solution make it a low competitive oxidizing agent. For this reason,  $\text{H}^+$  oxidation is reasonably the main reaction towards low potential elements in the case of strong acids (low  $\text{p}K_{\text{a}1}$ ) able to provide highly acidic solutions and/or when highly coordinative polydentate anionic species are formed by metal ion complexation, liberating low acidic  $\text{H}^+$  ions in solution. Based on the experimental evidences well supported by the described more formal studies, the classification in Class 1 and 2 of metal lixivants based on weak OAs has been proposed in Table 3 depending on the thermodynamic spontaneity of the metal oxidation reaction by  $\text{H}^+$ . OAs providing  $E^{\circ}{}_{\text{cell}}$  only slightly negative for the described process, may combine the two reactions, even more in non-standard conditions.

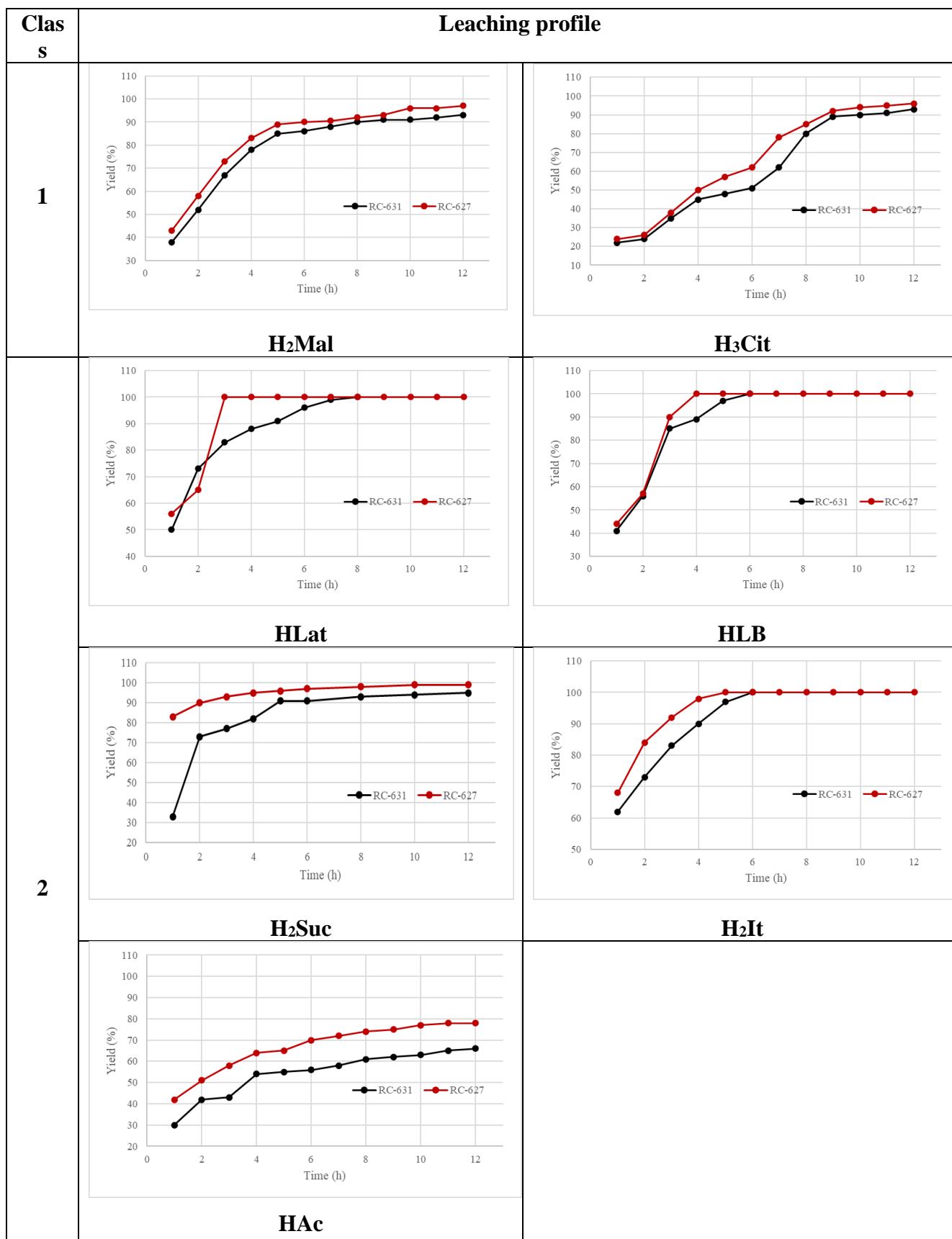
### 3.2 Leaching experiments on test specimen of HM powders

Leaching experiments on real WC-Co powders were carried out in the same conditions applied to Co metal powder. Specifically, 250 mL of 0.5 M aqueous solutions of H<sub>2</sub>Mal and H<sub>3</sub>Cit Class 1 OAs, as well as HLac, H<sub>2</sub>Suc, H<sub>2</sub>It, HLB and HAc Class 2 OAs were reacted in an open flask with 0.500 g aliquots of RC-627C and RC-631L test specimen, at room temperature under magnetic bar stirring. Fig. 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 leachates of the test specimens in time (1 h steps). The Co amount in the leachate was determined by ICP-OES measurements on digested measured aliquots of the solution, as detailed in Sect. S1.1.

As shown and expected under these experimental conditions, all the used acids demonstrated to be effective in cobalt dissolution from RC-627C achieving in most cases an almost complete Co-dissolution in short times, specifically 3 hours with HLac, 4 hours with HLB, H<sub>2</sub>Suc and H<sub>2</sub>It, 10 hours with H<sub>2</sub>Mal and H<sub>3</sub>Cit solutions, respectively. In the reported conditions, HAc demonstrated to provide the less effective leaching solution, achieving around 90% Co dissolution on RC-627C in 12 hours. Co-leaching on RC-631L demonstrated to be slightly less efficient than observed on RC-627C but still satisfactory, obtaining over the 90% Co-dissolution in 5 hours with HLac, HLB and H<sub>2</sub>It, 7 hours with H<sub>2</sub>Suc, 8 hours with H<sub>2</sub>Mal, and 9 hours with H<sub>3</sub>Cit solutions, respectively, while the HAc solution dissolves around the 65% of cobalt in 12 hours. This difference can be reasonably attributed to the lower values of the WC particles mean grain size and of the metallic binder mean free-path of the RC-631L test specimen, as found in previous studies on solvometallurgical processes on the same samples.<sup>18</sup> Additional characterization was performed on the solid residues after leaching to point out the stage of Co-dissolution and the state of the remaining W-based phases. In particular, powder X-ray diffraction (p-XRD) and SEM/EDS analysis were made on the RC-631L sample before and after leaching with several of the systems under study. These techniques, despite having a lower sensitivity with respect to the chemical analysis, demonstrated to be very diagnostic and fast tools for monitoring the reactions being able of pointing out the progress of the Co-leaching through the lowering of Co peaks without requiring any additional sample treatment for analysis. Furthermore, p-XRD is also diagnostic of the chemical form of the species.

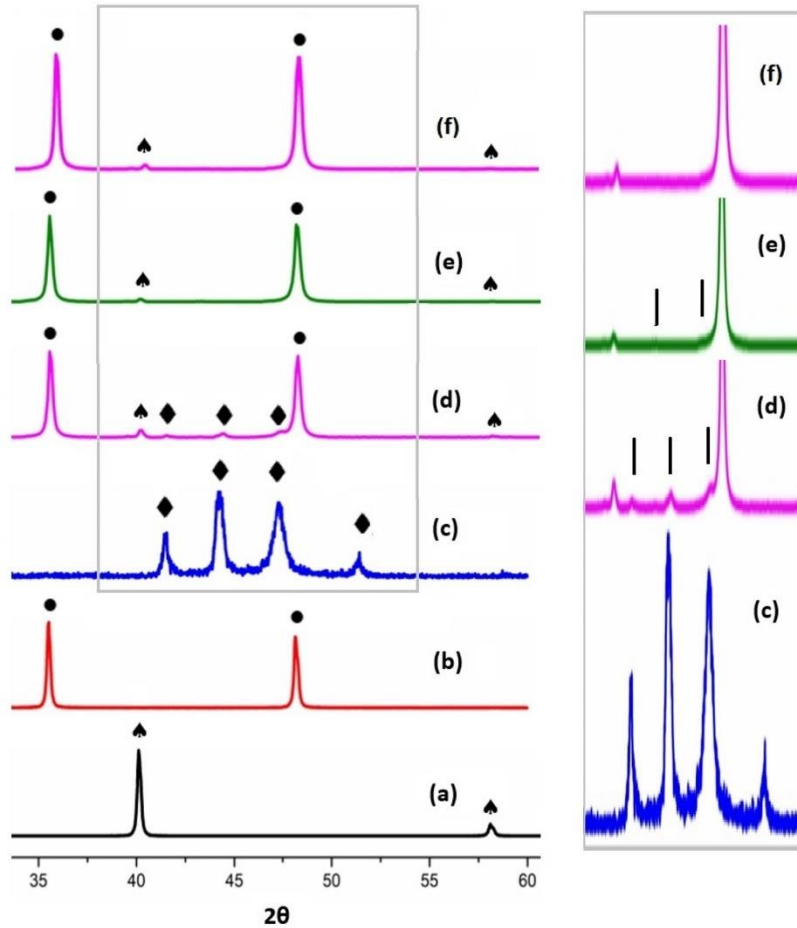
Figures 4 and S3 show respectively the p-XRD and SEM-EDS patterns recorded for the RC-631 L sample before and after leaching representatively with solutions of HLac and H<sub>2</sub>Suc for 4 and 6 hours, under the conditions reported above. The XRD patterns of the sample before (Fig. 4d) and after leaching (Figs. 4 e and f) clearly show the disappearance of Co metal peaks after treatment, highlighting the almost complete dissolution of cobalt in HLac and H<sub>2</sub>Suc solutions after 4 and 6 h leaching, respectively. Furthermore, the patterns collected after treatment showed no changes in the other parts of the spectrum in terms of the disappearance of existing species or the appearance of new peaks related to newly formed species. This evidence demonstrates the capability of the solutions of these acids to dissolve Co selectively leaving W and WC unreacted. In agreement, SEM-EDS characterization highlights an almost complete Co dissolution with a slightly different degree between the two experiments (99 wt.% and 98 wt.%, with HLac<sub>(aq)</sub> and H<sub>2</sub>Suc<sub>(aq)</sub> respectively, in line with the leaching profiles reported in Fig. 3), preserving both W and C presence.

These experiments demonstrate that the proposed method is able to tune the percentage of Co in the treated powders by tailoring appropriately the leaching time on the basis of the leaching profiles meeting the compositional requirements of the industrial hard metal manufacturing process. P-XRD and/or SEM-EDS characterization of the solid residue demonstrated an appealing and expeditious tool for the monitoring of the process evolution.



**Figure 3.** Co-leaching profiles from RC-627C and RC-631L recovery powders (0.5 g) on varying the leaching agent and times. Experimental conditions: [Acid] = 0.5 M; r.T. and pressure; stirring. Results

are reported as the average values of two different experiments.



**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-631L before Co-leaching; e) RC-631L after 6 h leaching with H<sub>2</sub>Suc; f) RC-631L after 4 h leaching with HLac. In the zoom, magnification of c), d), e) and f).

### 3.3 The HLac case study: set-up of operative conditions

#### 3.3.1 Liquid/Solid (L/S) ratio

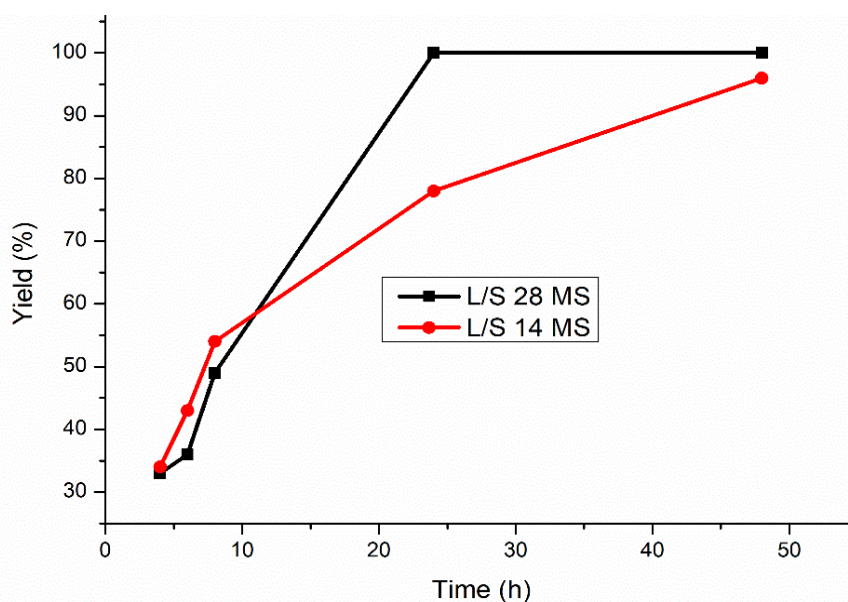
With the view of meeting industrial requirements for technological transfer and improving the sustainability of the process, experiments addressed to limit the amount of the leaching agent and solvent were performed on solutions of the most promising bio-derived acid, namely HLac. Specifically, attempts to fix the Co:Acid molar ratio to lower values than the previous 1:74 (0.5 g of test specimen approximately 20 wt. % Co; [Acid] = 0.5 M; Volume = 0.250 L), 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 with a 1 M solution at room temperature under magnetic bar stirring, monitoring the time of complete disappearance of Co powder from the reaction vessel. Table 4 summarizes Co-leaching yields and experimental conditions applied on Co-powder.

**Table 4.** Co-leaching in an open flask of 0.375 g Co powder by varying the Co:Acid molar ratio under magnetic bar stirring. [HLac] = 1 M. \*Calculated values referring to the corresponding amounts of WC-(20 wt. %)Co material.

L/S*	Volume (mL)	Co:Acid Molar ratio	Leaching time (h)
14	25	1:4	7-8
28	50	1:8	6
42	75	1:12	6

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 acid that allow the leaching to be almost quantitative in a short time. A further increase to 1:12 does not show a significant time reduction.

On these bases, 18.8 g of RC-631L sample were treated in an open vessel with 250 and 500 mL of HLac 1 M at room conditions under mechanical stirring. Figure 5 shows the Co-leaching profiles of the sample under the reported conditions (detailed Co-leaching yields are reported in Sect. S5, Table S9).



**Figure 5.** Co-leaching profiles on RC-631L sample shown as Co-dissolution yield (%) vs time (h) by varying L/S ratio (14 and 28) under mechanical stirring at room conditions.

As shown and expected based on the previous results, a 28 L/kg ratio, corresponding to a 1:8 Co:HLac molar ratio, allows a complete Co dissolution in a shorter time (within 24 hours), while longer times (at least 48 hours) are required when a 14 L/kg ratio, corresponding to a 1:4 molar ratio, is applied. Nevertheless, if an industrial point of view is considered, using a more favorable 14 L/S ratio may represents the best compromise for achieving appropriately tuned composition materials. Indeed, under the reported conditions a recovered powder with a WC-(5%)Co composition can be achieved in 24 h. It is worthy to note that the leaching times in these experiments were found longer than those found on Co-powder under the same conditions. Such an increase in the leaching time with the amount of starting material (0.375 g Co powder vs 3.75 g of Co in 18.8 g RC-631L) supported the hypothesis of a key role of dissolved oxygen in the reaction rate.

### 3.3.2 Studying the oxygenation effect on Co leaching by aqueous HLac solutions

To make the leaching process as much efficient as possible, tests were carried out to identify the most kinetically favored reaction, specifically by:

Trial 1. Determination of the H<sub>2</sub> produced, by gas chromatography (GC) measurement in the absence (a) and in the presence (b) of oxygen;

Trial 2. Effect of forced oxygenation on leaching times of metallic cobalt, by blowing air into the reaction environment.

The tests were carried out using a commercial HLac aqueous solution at room temperature and under magnetic stirring. In test a) of the Trial 1, the leaching solution was previously de-aerated by means of a flow of gaseous N<sub>2</sub>. In test b) the reaction was allowed to proceed in the presence of dissolved oxygen and the one present in the head space. During test a), conducted in the absence of oxygen, a quantity of H<sub>2</sub> is produced that is more than 60% higher than that produced during test b) in the presence of O<sub>2</sub>. This indicates that in limiting conditions, characterized by little or no presence of oxygen, the reaction with the production of hydrogen is favored; but it also indicates that oxygen has some influence on the reaction. This influence was investigated in Trial 2, in which the time associated with the quantitative leaching of the metal cobalt powder in the absence and in the presence of forced oxygenation and maintaining the same operating conditions as Trial 1, were compared (Table 5). The test in natural oxygenation conditions was carried out in the absence of air blowing; the forced oxygenation reaction was carried out by bubbling pressurized air through a thin tube into the reaction medium. The complete disappearance of the Co powder indicates the end of the reaction.

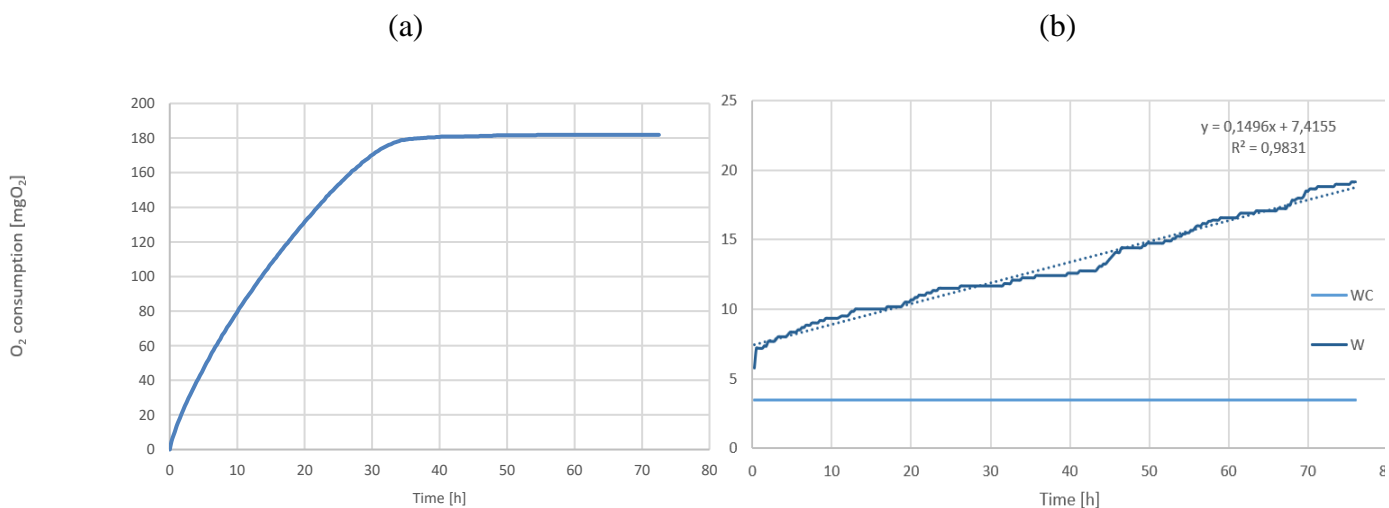
**Table 5.** Effect of the oxygenation (forced aeration by blowing air through a thin glass tube) on the metallic cobalt leaching time.

V (mL)	[HLac] (M)	Co (mg)	pH	Leaching time (h)	
				Naturally dissolved O <sub>2</sub>	Forced aeration
50	1	357	1.7	13	3-4

As shown, significantly shorter times were found for Co-leaching experiments performed through forced aeration, confirming the relevant effect of O<sub>2</sub> on the reaction.

On these bases, additional experiments addressed to point out the entity and kind of interaction of oxygen with the components of the real WC-Co powder, were carried out on Co, W and WC powders using a Sapromat respirometer as detailed in Sect. 2.2.4.

Figure 6 shows the profiles of oxygen consumption vs leaching time determined by respirometry of the O<sub>2</sub>-dependant HLac leaching reactions.



**Figure 6.** Leaching reaction with 0.1 L of HLac 1 M under Sapromat respirometer conditions: oxygen consumption curve of a) Co metal (0.714 g); b) WC and W powders (2.86 g).

As shown, cobalt powder consumes oxygen during the leaching reaction. The monitoring of oxygen consumption by Co allows to estimate the end of the reaction, represented by the achievement of the plateau of the curve in Fig. 6a (HLac solution does not consume oxygen). Despite longer leaching times (approximately 30 h) were found using this method,<sup>2</sup> it points out some relevant aspects of the leaching reaction. Specifically, the amount of oxygen consumption (mg O<sub>2</sub>) during the reaction almost reflected the stoichiometric need: in the face of 193 mg O<sub>2</sub> theoretically required by the reaction (0.27 g O<sub>2</sub>/g Co), 180 mg O<sub>2</sub> were consumed during the experiment, confirming the primary role of O<sub>2</sub> in the leaching reaction. Experiments carried out at various pH values, obtained by adding a controlled amount of NaOH(aq) to the leaching solution, pointed out that at pH above 4.5, the formation of abundant precipitations (oxides and hydroxides of Co(II) and (III)), occurred in agreement with the literature.<sup>19</sup> Against, pH < 4.5 prevented oxides and hydroxides formation allowing the reaction to occur efficiently towards [Co(Lac)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] complex formation. This is a key point, because the formation of insoluble by-products is undesired in selective leaching processes. Against, tungsten does not consume oxygen. Tungsten carbide, on the other hand, consumes a small and linearly increasing amount of O<sub>2</sub> reaching 12.5 mg O<sub>2</sub> value (0.145 mg O<sub>2</sub>/g WC h) after 30 hours (average leaching time found for cobalt powder). This finding, that should be taken into account assessing global O<sub>2</sub> consumption during the process on WC-Co real material, confirms the knowledge of slow but occurring oxidative phenomena involving WC.





Finally, further leaching tests were performed for defining the best oxygenation system. Jar test reactions were carried out on metallic cobalt powder (1.47 g Co, 1 M HLac 0.2 L, r.T, mechanical stirring) with air blowing through the solutions by a thin glass tube providing large

<sup>2</sup> Sapromat respirometer works in a "static" mode, supplying parceled amounts of oxygen in the head space of the closed reactor. This delivering mode does not favor, from a kinetical point of view, the oxygen availability for the leaching reaction, resulting in longer leaching times with respect to those recorded even just in an open flask.



bubbles and, for comparison, a porous stone providing fine bubbles, both powered by a small air compressor. Table 6 summarizes conditions and leaching yields for the two systems after 4 hours. Each experiment was performed twice.

**Table 6.** Cobalt (1.47 g) leaching efficiency with HLac (1 M, 0.2 L) under large and fine bubble aeration. \*Determined by ICP-OES on the leachate and obtained as average values of two independent experiments.

Aeration system	Leaching systems		Leaching yield [%]*
	$t_0 = 0 \text{ h}$	$t_1 = 4 \text{ h}$	
Large bubbles			62
Fine bubbles			92

As shown and expected, the fine bubble system is significantly more efficient and achieves an almost complete leaching of Co in the observation time. These results were also confirmed by increasing the scale of the experiment, obtaining an almost quantitative Co dissolution in 4-5 hours by treating 2.94 g and 5.89 g of Co powder with 0.4 and 0.8 L of HLac 1 M, respectively. This result suggests presumably the fine bubble diffuser provides available oxygen at a rate compatible with its consumption by the reaction.

### 3.3.3 pH effect on the leaching reaction

In addition to the oxygenation, the leaching reaction is influenced by pH as it affects the Co and O<sub>2</sub> reduction potential as well as the produced species by the reaction. For this reason, an experiment was conducted to compare the leaching behavior of metallic Co powder at different pH values. The experiments were carried out using a Co:HLac molar ratio of 1:8 and it was observed that:

- the leaching reaction does not take place in a strongly alkaline environment;
- at weakly acidic pH values (> 4.5) the leaching reaction is accompanied by the formation of abundant precipitates (Co(II) and (III) oxides and hydroxides) as known from the literature;<sup>31</sup>
- at pH ≤ 4 the reaction takes place without the formation of poorly soluble by-products.

Based on the above, leaching cobalt for HM in the presence of fine bubble oxygenation and an acid environment with a pH ≤ 4 were selected as the optimal conditions for applicative purposes.

### 3.4 Scale-up of the leaching process by HLac on WC-Co residues

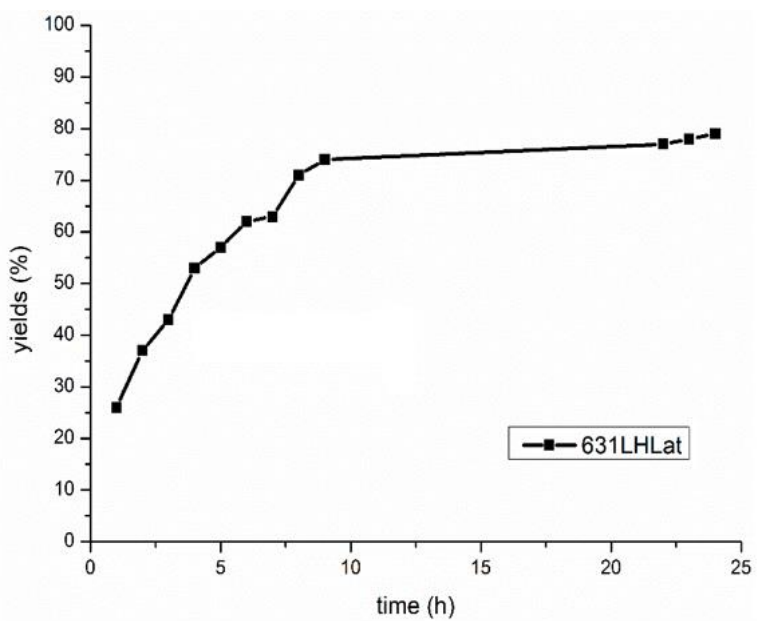
A leaching experiment on 650 g of RC-631L powder in the presence of forced aeration was performed with a HLac solution (1 M, 7 L, L/S = 14 for limiting the amount of solution) into a 30 L mixing vessel. Stirring was provided by bubbling air from the bottom of the vessel through spherical porous stones connected to an air compressor. Leaching reaction was monitored for 24 hours by sampling the leachate and analyzing the cobalt content of the digested aliquots by ICP-OES as detailed in Sect. 2.2.3. The Co-leaching set-up and profile of this experiment are shown in Figure 7.

Under the above conditions, approximately the 80% yield of Co dissolution was achieved in 24h. This data fully agreed with the corresponding ICP-OES characterization of the digested solid sample where a WC-(5.7%) Co composition was found. Furthermore, these results were supported by XRD and SEM/EDS solid state characterization on the recovered powder which highlighted the lowering of cobalt peaks and a residual amount of cobalt in the final mixture (See Figures S4 and S5).

a)



b)



Leaching time (h)	Yield (%)
1	26
2	37
3	43
4	53
5	57
6	62
7	63
8	71
9	74
22	77
23	78
24	79

**Figure 7.** Co-leaching scale-up experiment on RC-631L powder (650 g) with HLac (1 M, 7 L) under aerated conditions. a) Forced aeration set-up in a thermostated double-wall 30 L mixing vessel equipped with motovariator for mechanical stirring, pH control and distillation line; b) Co-leaching profile.

### 3.5 Quality assessment of the WC-Co recovered powder

C and O content in the WC-Co powders suitable to be directly employed in HM manufacturing is a critical parameter for obtaining HM tools with performing properties. Indeed, it is well-known that the co-presence of C and O into a WC-based powder lower the C content of the mixture during the sintering phase due to  $\text{CO}_x$  formation, affecting the final properties of the HM material due to the occurrence of the so-called  $\eta$ -phase in the final material.<sup>10</sup> C and O elemental analysis were, hence, performed as detailed in Sect. S1.2 on the solid residue of the leaching experiment (Sect. 3.4), with the view to check the quality of the recovered material for applicative purposes. The measured C and O composition – 6.24 and 1.60 wt. %, respectively – were found higher than the optimal 5.70 and  $\leq 0.40$  wt. % values. The most critical aspect is the significantly high amount of oxygen typically found for WC-Co powders treated in water where hydration phenomena of the WC-surface may occur beside the oxidative phenomena pointed out through respirometry experiments. Also, the retention of unwashed organic leaching agents/complexes may occur, affecting C-O elemental analysis. Thus, a thermal treatment under an inert environment (1000 °C, 2 h,  $\text{N}_2$ ) was attempted for improving the quality of the powder. The thermal treatment demonstrated to be able of driving powders composition within the desired ranges as the new material showed a C 5.65 wt. % and 0.19 wt. % composition, and to make it suitable for HM production.

## 4 Conclusions

A selection of OAs was tested as leaching agents for Co metal, both in the form of metal powder and involved in a composite material like WC-based cemented carbide where it plays the role of the metallic binder. All the selected OAs, namely  $\text{H}_2\text{Mal}$ ,  $\text{H}_3\text{Cit}$ ,  $\text{HLat}$ ,  $\text{H}_2\text{Suc}$ ,  $\text{H}_2\text{It}$ ,  $\text{HLB}$  and  $\text{HAc}$ , demonstrated to work well achieving a quite fast and selective almost quantitative Co dissolution in aqueous solution at low concentration level and room conditions. Besides, a relevant role of oxygen in the leaching reaction with several of these acids was found, highlighting different capabilities among the selected OAs to oxidize the metal. Experimental evidences and computational calculations of normal reduction potentials of cobalt and  $\text{H}^+$ , taking into account the  $K_{a1}$  of the acid and the  $K_f$  of the corresponding Co-complex, agreed in identifying two classes of leaching agents: Class 1, which consists of OAs where  $\text{H}^+$  is thermodynamically favored to work as oxidant towards Co; Class 2, which instead consists of OAs where the metal oxidation is mainly carried out by external oxidants, e.g. dissolved  $\text{O}_2$ , being the oxidation through  $\text{H}^+$  thermodynamically unfavored. Due to the high appeal related to the use of bio-derived eco-friendly OAs in hydrometallurgy, these insights are crucial in the selection of the most appropriate OA for the specific application as well as in designing the leaching process. Furthermore, this model is in principle applicable to all Metal-OA combinations becoming a key tool for OAs leaching behavior prediction. Herein the application of OAs leaching solutions to Co-containing hard metal powders was used as a successful case study addressed to the industrial recovery of critical raw materials. Among the selected acids particular attention was devoted to the use of  $\text{HLat}$  in hydrometallurgy because its effectiveness, low cost, sustainability and large availability through biotechnological fermentative processes. A systematic study of the process conditions was carried out with satisfactory results, showing the capability of the leaching solution to provide in mild conditions good quality recovered products suitable for re-employment in HM manufacturing.

## 5 Acknowledgments

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22 action [MC's mobility]; the Italian Ministry for the Environment, Land and Sea Protection [CoW\_aste project, 2019]; Fondazione di Sardegna ["Precious metal-free complexes for catalytic CO<sub>2</sub> reduction" project, 2017]; the FILMS corp. ["The selective extraction of excess cobalt from the recovery powders of the "hard metal" production process" project, 2018; "The selective extraction of excess cobalt from the powders produced by carbothermal regeneration of "hard metal" scrap" project, 2019].

## 6 Supplementary Material

The Supplementary Material for this article is available free of charge at... CCDC 2259119 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif), or by emailing [data\\_request@ccdc.cam.ac.uk](mailto:data_request@ccdc.cam.ac.uk), or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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