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SELECTIVE LEACHING OF Co AND W FROM HARDMETAL WASTE USING LACTIC ACID ACROSS A WIDE COMPOSITIONAL RANGE

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ABSTRACT

The recovery of Critical Raw Materials (CRMs) is a strategic priority for the metallurgical industry. Hardmetal (HM, WC–Co) production is particularly vulnerable to tungsten (W) and cobalt (Co) supply shortages and price volatility, as these elements constitute its primary feedstocks. This study investigates valorization strategies for HM waste through a combined thermal–chemical approach. Oxidized powders (70.18% W, 8.41% Co, as WO_3/$CoWO_4$) obtained from WC–Co scraps by thermal oxidation underwent leaching for 6 h at 100°C (L/S = 5 L/kg) with 4 M lactic acid/lactate solutions at pH 1–8, and with HCl (pH < 1) and NaOH (pH 14) alone as limits, with particular focus on the dissolution behavior of W and Co. Co dissolution was highest in HCl alone (57.99%, W ≈ 0%) and fell below the detection limit from pH ≈ 5 onwards, whereas W dissolution was quantitative at pH 14, the only metal dissolved at pH 6–8, and 38.59% (Co 9.17%) at pH 4. Composition beyond pH also mattered: replacing HCl with HNO_3 lowered Co dissolution from 57.99 to 9.62% (acid alone) and from 14.08 to 5.31% (pH 1, lactate), while W rose from 3.32 to 8.48% in the latter. Fixing I = 3.4 M left the chloride-only test unchanged but lowered Co to 3.13% in the HCl–lactate mixture, and shifted the chloride-free pH 4 test only modestly (Co 9.17 → 6.84%), pointing to a chloride-specific interfacial effect rather than bulk Co(II) speciation. Thus, the systematic evaluation of leaching performance across pH and solution composition provides key insights into metal selectivity and process optimization. The results contribute to the development of a smart and sustainable recycling strategy for efficient W and Co recovery from industrial HM waste streams.

1. INTRODUCTION

Hardmetals (HMs), also known as cemented carbides, are sintered materials composed of hard tungsten carbide (WC) particles bonded together by a metallic binder, typically cobalt (Co). Since 2011, W and Co have been classified by the European Union as Critical Raw Materials (CRM) due to their high economic importance and supply risk (European Commission. Joint Research Centre., 2017). In 2022, HM manufacturing accounted for about 65% of global W demand (Zeiler, 2022) and 5% of Co demand (Fisher H., 2023). Beyond HM applications, W is widely used in alloyed steels and superalloys (Zeiler et al., 2021), while Co demand is rapidly increasing due to its key role in Li-ion batteries (Fisher, H., 2022). These factors enhance the criticality and market value of both metals, making HM waste an attractive secondary resource within a circular economy model encouraged by European Directives (EU Directive 2018/850; EU Directive 2018/851).

Metal recycling is already partially implemented in the HM value chain through chemical and direct processes. Chemical recycling involves a deep transformation of scrap materials providing high-purity products, but suffers from high energy consumption, hazardous reagents, and significant wastewater generation (Lassner and Schubert, 1999; Kumar et al., 2023; Zeiler et al., 2021; Kuşdemir et al., 2022,). Direct methods, with the zinc process as the most industrially remarkable example (Srivastava et al., 2019), consist of a series of chemical and/or physical treatments capable of destroying the hard structure of the scrap, followed by a thermal remanufacturing of the recovered powder. They are less resource-intensive, but limited in versatility and in the range of suitable waste streams (Katiyar & Randhawa, 2020a; Zeiler et al., 2021).

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An alternative process performed at the OMCD TEK HUB S.p.A. on hard scraps may involve a sequence of thermal Oxidation, Reduction and Carburization phases. The so-called ORC process can transform the hard material into a product easy to powder, producing an oxidized powder (named POX by the company) primarily consisting of WO_3 and $CoWO_4$. POX, then, can undergo a thermal reduction under H_2 atmosphere from which W/Co powder (named REW) is obtained. Finally, a thermal carburization of REW powder in the presence of an appropriate amount of carbon black provides a recycled WC-Co powder (named OXR) ready to be sintered for the production of new tools (Lassner and Schubert, 1999; Katiyar and Randhawa, 2020b).

Although the global recycling rate of end-of-life WC products reached 46% per year, further efforts are required to reduce the environmental footprint of current technologies, as well as the dependence of HM manufacturing on global suppliers of W and Co primary resources (Zeiler et al., 2021). In this context, organic acids have emerged as promising leaching agents for low-reduction-potential metals (Cera et al., 2023; Golmohammadzadeh et al., 2018; Seo and Kim, 2016). The biological production of a variety of organic acids from agro-industrial by-products and wastes represents a particularly appealing and environmentally friendly alternative to traditional chemical conversion processes starting from petroleum-based precursors (Schneider et al., 2019). Their effectiveness towards Co (the typical binder material in hardmetals) and W (carbide-phase primary constituent) strongly depends on their metal oxidation state: while tungsten remains largely inert in WC–Co materials, cobalt can be selectively dissolved under mild conditions; conversely, in oxidized powders, both W and Co can be efficiently leached (Cera et al., 2025; Oumarou Amadou et al., 2021, 2023).

Based on these principles, the University of Cagliari and OMCD TEK HUB S.p.A. developed a new recovery route combining the ORC thermal treatment with an eco-friendly, organic acid-based leaching strategy (BioCR), aimed at improving both sustainability and versatility in HM recycling. The versatility of the approach lies in the different efficiency and selectivity of organic acid mixtures in metal dissolution and recovery as the experimental conditions are varied, with a key reference to the feeding material (e.g. WC-Co or WO_3-$CoWO_4$) and to pH, for a specific semi-finished fraction. As a specific example, here is described and discussed a systematic study on the valorization of oxidized HM powders (POX) from the ORC process by using low-cost, bio-derivable and degradable lactic acid (HLac) solutions. Specifically, the study investigates the different behavior of metals (Co and W) towards a leaching mixture containing a complexing agent (Lac^-) at different pH values. Among organic conjugate acid-base systems, HLac/Lac^- was selected because it is safe and biodegradable, and because leaching solutions at different pH can be easily bio-derived from dairy waste through a controlled lactic fermentation (Serpe et al., 2023). Taking as the main reference (pH = 4) a 4 M HLac/Lac^- buffer solution that proved to be efficient in Co and W leaching from POX powders in previous studies (Cera et al., 2025), the screening will range from strongly acidic to strongly alkaline solutions, varying the pH by means of HCl or NaOH addition. Results showed an almost perfect selectivity towards Co and W respectively at the acid and alkaline extremes of the investigated pH range, with a relevant contribution of the conjugate HLac/Lac^- system to tailor the W/Co leaching rates for pH ranging from 1 to 6. The importance of this investigation lies in the rational use of customized leaching mixtures containing organic conjugate systems for Co and W valorization from oxidized fractions, pursuing good results in terms of recycling rates of valued metals and quality of the recovered products for manufacturing, limiting environmental impact and use of petroleum-derived chemicals. This organic-acid-based approach is one of several emerging low-reagent alternatives for Co/W recovery from hardmetal scrap, alongside electrochemical and electrodialytic separation routes (Lo et al., 2023; Guedes et al., 2024), with a specific focus on POX feed investigated (WO_3/$CoWO_4$) and to the pH and solution-composition range tested.

These processes are under further investigation in the framework of the ongoing Horizon Europe RESQTOOL project, aimed at recycling high-quality CRM resources from machining tools for re-use applications.

2. MATERIALS AND METHODS

2.1 Materials

All chemicals were of reagent grade and used as purchased by CARLO ERBA Reagents without any purification: L(+)-lactic acid, 88-92%; hydrochloric acid solution, 37%; nitric acid, 65%; sodium hydroxide pellets, ≥ 97%; sodium nitrate, ≥ 99%. 2 M HLac/Lac^- buffer was prepared by neutralizing half of a 4 M HLac solution with NaOH pellets (2 M NaOH). Solutions with pH = 1 and with pH = 6 and 8 were prepared by adding HCl (37%) or NaOH (pellets), respectively, to the HLac (aq) solution, monitoring the pH value with a pH-meter (Thermo Scientific Orion VersaStar Pro), and diluting with distilled water to the desired volume when the heat was dissipated and the solution reached room temperature. POX powders were provided and produced by OMCD TEK HUB S.p.A. (OMCD Group, Anzola d'Ossola, VB, Italy).

2.2 Chemical characterization of POX and leachates

POX are green-blue powders obtained after a thermal oxidation process of HM scraps at 800-950°C under air flow. The chemical composition of POX powder was indirectly determined by analysing the sample post thermal reduction (corresponding REW powder) and calculating the metal content in POX, considering the oxygen loss during the reduction phase, as shown in the following Equation (1):

$$Me\ content\ in\ POX\ (wt.\ \%) = \frac{Amount\ of\ Me\ in\ 100\ g\ REW}{123\ g\ POX} \times 100 \quad (1)$$

Where Me is the metal under study; the "Amount of Me in 100 g REW" is obtained by Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES, Perkin Elmer Optima DV 7000) analysis of the digested REW sample; "123 g POX" is the POX mass corresponding to 100 g REW after oxygen loss, determined at the OMCD TEK HUB as a mean value from several experimental measurements.

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For analytical purposes, 0.1 g REW powder aliquots were digested in TFM (Tetrafluoroethylene-perfluoropropyl vinyl ether) vessels with mixtures of HNO_3 (65%, 5 mL), H_2SO_4 (96%, 3 mL) and HF (40%, 2 mL) in a Milestone Ethos 1 Microwave digester, equipped with HPR1000/10S high-pressure segmented rotor, ATC-400CE automatic temperature control and Terminal 640 with easyCONTROL software. The treatment was performed applying a microwave program consisting of two steps lasting 15 and 20 minutes each, at 200°C and microwave power up to 1000 W. The samples were prepared for analysis by diluting the digested sample with 1% HNO_3 (aq) and then, the metals were determined by ICP-OES, with respect to a 5-point calibration plot in the 0.01-10 ppm range for each metal under investigation. The freshly prepared solutions were analyzed via ICP-OES for Co and W, as well as for other relevant metals. The chemical characterization of POX was then found to be W (70.18%), Co (8.41%), Cr (0.40%), Fe (0.10%), Al (0.01%), and Ti (0.01%).

Physical-chemical characterization of the POX powder was performed by X-Ray diffraction by means of a Rigaku Geigerflex D-Max diffractometer operating with Cu tube at 30 kV and 30 mA and mineral identification was carried out by comparison with the JCPDS File 1985. P-XRD patterns confirmed that the POX composition matched the expected mixture of WO_3 and $CoWO_4$ with no evidence of other phases.

2.3 Leaching experiments design and procedures

Previous studies (Cera et al., 2025) have shown that a 4 M HLac solution at pH 4 (i.e. 2 M lactic buffer) and 100°C works effectively in dissolving both Co and W, while strong inorganic acids and bases proved to be completely selective towards Co and W. Based on these results, it was decided to investigate the effect that solutions with similar composition but different pH values could have on the selectivity of leaching the two metals.

Leaching solutions to test and compare from one to another were prepared by adding appropriate HCl or NaOH amounts to a 2 M HLac/Lac^- buffer solution, obtaining three lower and three higher pH values with respect to the buffer taken as a reference, as summarized in Table 1. The choice of pH values was taken as follows:

- Exp. 2, pH = 1. pH values ≤1 allow W precipitation as $WO_3 \cdot H_2O$ and increase the Co dissolution rate
- Exp. 3, pH = 1.4. It is the natural pH of a 4 M HLac solution
- Exp. 4, pH = 4. The lowest pH obtainable by a controlled bio-lactic fermentation process
- Exp. 5, pH = 6. The optimal pH for a highly efficient bio-lactic fermentation process
- Exp. 6, pH = 8. pH values ≥7 allow high-rate WO_3 leaching and promote Co precipitation as low-solubility hydroxides and oxides
- Exp. 1 and 7, pH < 1 and pH = 14. They were considered as representative of solutions at the extreme conditions, prepared with the same amount of HCl/NaOH as in Exp. 2/6, but with no HLac or Lac^- added.

Leaching reactions were performed in triplicate in the Radleys reaction station Mya4 on about 40 g of POX powder and 200 mL of leaching solution, at refluxing temperature (100°C), under mechanical stirring at 250 rpm, and with a liquid-to-solid (L/S) ratio of 5 L/kg, by varying acid and base concentration and final pH. The different conditions tested for the leaching reactions are reported in Table 1.

Further experiments were performed:

- at the fixed ionic-strenght (I) 3.4 M (obtained by appropriate $NaNO_3$ addition to the mixtures);
- using same equivalents of HNO_3 in place of HCl

in order to assess the effect of I and of the complexing behaviour of the anion on the metal leaching efficiency and selectivity.

The amounts of Co and W in the leachate were determined by ICP-OES on measured aliquots of the solution, as detailed above.

Leaching yields reported throughout the manuscript are calculated using Equation 2:

$$Yield_{Me}\,(\%) = \frac{Amount\ of\ Me\ in\ the\ leachate\ (g)}{Amount\ of\ Me\ in\ the\ test\ specimen\ (g)} \times 100 \qquad (2)$$

Where Me is the metal under study; the "Amount of Me in the test specimen" is calculated starting from the characterization of the sample, and the "Amount of Me in the leachate" is obtained by ICP-OES analysis of the leachate.

TABLE 1: Leaching mixtures used in this study. *It considers lactate concentration. HLac/Lac- speciation relates to the final pH. *'2 M lactic buffer. **pH values are reported as read from the pH-meter at room temperature and approximated to consider the acid and base concentrations >1 M. The associated uncertainty is expected to be a few tenths of a pH unit for Experiments 2–6, and larger and not thermodynamically well-defined for the two extreme, unbuffered conditions (Experiments 1 and 7); it affects only the pH value used as a label, not the acid/base/lactate composition of each mixture, which is fixed by preparation (Table 1) and is what is systematically varied between experiments.

Experiment name	HLac/Lac^- [M]*	HCl [M]	NaOH [M]	Final pH**
1	-	2.1	-	<1
2	4	2.1	2	1
3	4	-	-	1.4
4 (Reference)	4*'	-	2	4
5	4	-	3.2	6
6	4	-	3.4	8
7	-	-	3.4	14

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Molar ratio (%) of metals is calculated using Equation 3:

$$\chi_{Me(1,\ 2)}(\%) = \frac{in\ the\ leachate\ (mol)}{Amount\ of\ Me(1) + Me(2)\ in\ the\ leachate\ (mol)} \times 100 \quad (3)$$

where Me(1, 2) is the metal under study (Co or W).

3. RESULTS AND DISCUSSION

3.1 Leaching results

Figure 1 reports the cobalt and tungsten dissolution yields (calculated by Equation 2) obtained by treating aliquots of the POX powder (W 70.18%, Co 8.41%, present primarily in the form of WO_3 and $CoWO_4$) with leaching mixtures prepared as described in Table 1 and reacting for 6 h under refluxing and stirring conditions (see details in Sect. 2.3).

As expected and shown, $CoWO_4$ is more prone to leach at lower pH values, while WO_3 shows the opposite behavior, being preferentially leached in the most alkaline solutions. This behavior is particularly evident for the experiments at extreme conditions. In fact, Exp. 1 shows the highest value of dissolution efficiency for Co (57.99%) and the lowest for W (close to 0%), while Exp. 7 results appear reversed, with the highest dissolution for W (quantitative) and the lowest for Co (close to 0%). Co dissolution is substantial only under the more acidic conditions (Experiments 3-4, pH 1.4-4), while it drops to values indistinguishable from zero (below the ICP-OES limit of detection) from pH ≈ 4.5-5 onward (Experiments 5-7), consistent with the expected precipitation of Co oxide/hydroxide phases under these less acidic conditions (see Section 3.2 and Figure 3 for a speciation-based discussion). A certain degree of W dissolution can nonetheless be observed in Exp. 2 and 3, in which pH is close to 1 and W is expected to precipitate as $WO_3 \cdot H_2O$.

In more detail, Figure 2 shows the molar ratio (%) (calculated by Equation 3) of leached Co and W found in the solution for each experiment.

These results demonstrate how carboxylates, easily bio-derived and largely biodegradable, may work as leaching agents for W(VI) under much less harmful and milder conditions (pH 6) than strong alkaline mixtures (pH 14), while achieving comparable leaching yields and selectivity. On the other hand, the W/Co leaching ratio can be appropriately tailored by tuning the pH of the mixture. It is worth noting that complete selectivity towards Co is difficult to achieve on POX in the presence of HLac. This behavior can be attributed to the lower reactivity of Co(II) in the thermally obtained $CoWO_4$, compared with Co(0) in the reduced WC-Co material, as well as to the complexing action of Lac^- towards W(VI), even at acidic pH, which stabilizes the Co counterion, WO_4^{2-}, in solution, preventing $WO_3 \cdot H_2O$ precipitation. Looking at these results within the framework of the reactivity of W and Co in the different chemical forms they take across the semi-finished fractions of the ORC process – specifically, $WO_3/CoWO_4$ in POX, W/Co in REW, and WC/Co in OXR – OXR powders represent the most suitable feeding material when full selectivity towards Co is desired. Indeed, an efficient and fully selective reactivity of Co metal contained in these powders was found using $HLac/Lac^-$ buffer even in low-concentration solutions (0.50 M) at room temperature (Oumarou Amadou et al., 2023).

3.2 Cobalt(II) speciation and the stability of lactate complexes

To assess over what pH range Co(II) could plausibly remain in solution as a lactate complex despite the thermodynamic tendency of Co(II) to hydrolyze and precipitate as $Co(OH)_2(s)$, a Co(II) species-fraction diagram was calculated as a function of pH at 25 °C and an ionic-strength I ≈ 3.4 M (fixed with $NaNO_3$, matching the leaching medium; Figure 3). The model combines Co^{2+} hydrolysis ($CoOH^+$, $Co(OH)_2(aq)$) and $Co(OH)_2(s)$ solubility, from the recommended thermodynamic parameters of Ziemniak, Goyette and Combs (1999), together with Co-lactate complexation ($CoLac^+$, $Co(Lac)_2(aq)$).

The stoichiometry and stability of the Co(II)-lactate complexes were established in our own prior work (Oumarou Amadou et al., 2023): the isolated solid product $[Co(Lac)_2(H_2O)_2]$ confirms a 2:1 (lactate:Co) coordination, and its Supplementary Material (Table S2) reports log $\beta_1([CoLac]^+)$ = 1.39 and log $\beta_2([Co(Lac)_2])$ = 2.37 (I = 0.1 M,

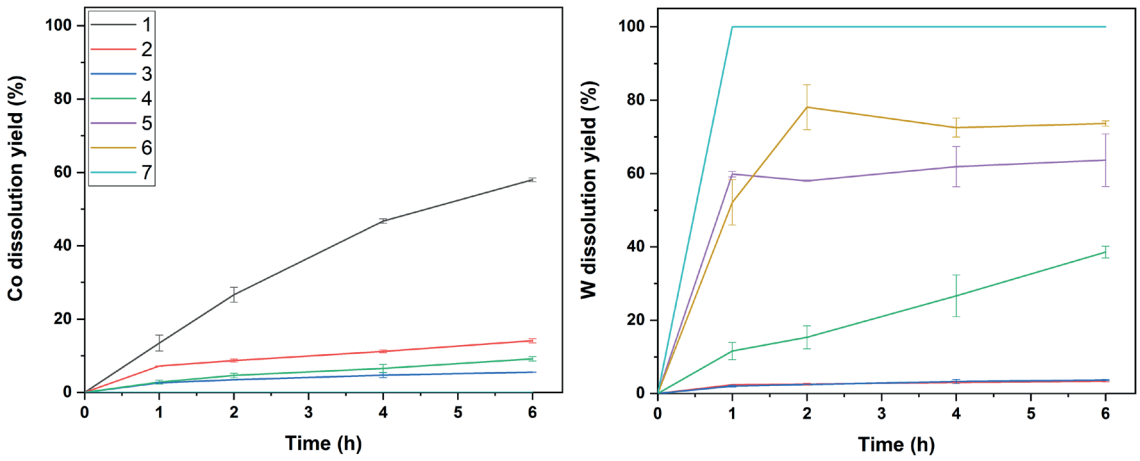


FIGURE 1: Co (left) and W (right) dissolution yield trend after 6 h at refluxing reaction temperature with 1-7 leaching mixtures as in Table 1. In the graph of Co, the trends of Exp. 5-7 are not represented because the corresponding Co concentrations were below the ICP-OES limit of detection (i.e., values indistinguishable from zero), while in the graph of W, trend of Exp. 1 is superimposed with the x-axis.

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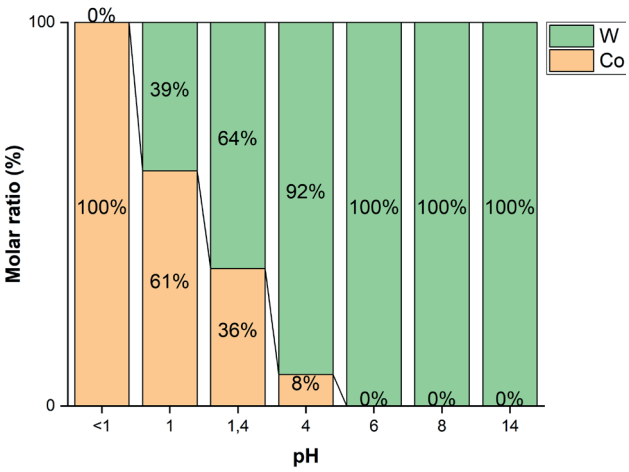


FIGURE 2: Molar selectivity of the leaching process: percentage of Co and W among the total moles of metal dissolved in each experiment (Experiments 1-7, Table 1), calculated from Eq. 3. Values are single-determination measurements, recalculated here from the ICP-OES data; see Section 3.3 and Figures 5-6 for replicated (n = 3) measurements on Experiments 1, 2 and 4.

25 °C), traced to the NIST Critically Selected Stability Constants of Metal Complexes Database (Smith, Martell and Motekaitis, 2004), together with pK_{a1}(lactic acid) = 3.67 from the same source. Ionic-strength correction from the tabulated I (0.1 M) to I = 3.4 M uses an extended Debye-Hückel/Davies-type expression in the same form used by Ziemniak et al. (1999, their Eq. 15); given that this extrapolation is applied roughly sevenfold beyond its documented validity range (~0.1-0.5 M), it should be regarded as a qualitative rather than quantitative guide to the speciation trends.

More rigorous ionic-strength correction schemes exist in principle, and for the free Co^{2+} ion specifically some are backed by genuinely Co-specific, directly-fitted (rather than by-analogy) experimental parameters. Bromley's (1973) own compilation for the Bromley-Zemaitis equation (Bromley, 1973; Zemaitis et al., 1986; reviewed by Balomenos et al., 2006) lists a directly-fitted individual-ion parameter for Co^{2+} (B = 0.0490, δ = 0.210) and salt-specific parameters for $CoCl_2$ (B = 0.1016) and $Co(NO_3)_2$ (B = 0.0912), documented to I = 3 mol/kg, i.e. closely approaching, though not quite reaching, the I = 3.4 M of the present leachates. The Specific Ion Interaction Theory (SIT; Grenthe and Puigdomènech, 1997) is likewise documented as reliable to substantially higher ionic-strengths than the Davies equation, and the full Pitzer ion-interaction model (Pitzer, 1973) is, in principle, the most rigorous approach for concentrated electrolytes; Millero and Hawke (1992) similarly tabulate Pitzer single-ion parameters for the free Co^{2+} ion itself (in Cl^-/ClO_4^- media), which are likewise more reliable at high ionic-strength than a Davies-type extrapolation. However, none of these more elaborate treatments could be applied here in a fully consistent way: doing so would require ion-interaction parameters specific to the Co(II)-lactate complexes ($CoLac^+$, $Co(Lac)_2(aq)$) at high ionic-strength, which, to the best of our knowledge, are not available in the literature for the Bromley, SIT, or Pitzer formalisms alike. Correcting only the free-Co^{2+} term with Bromley- or Pitzer-derived data while retaining a Davies-type correction for the lactate-complexation equilibria that dominate the diagram would produce an internally inconsistent hybrid model rather than a genuine improvement. Moreover, a recent analysis of a comparable protonation-equilibrium system, using a substantially richer ionic-strength dataset than available here, shows that even a Pitzer-type treatment risks over-parametrization when the underlying experimental data are insufficient to constrain its additional terms (Cappai et al., 2026). We therefore retain the single-parameter Davies-type extrapolation throughout the present model, consistent with the common practice of using simpler ionic-strength corrections when system-specific, higher-order interaction parameters cannot be independently verified (Balomenos et al., 2006) but considering the qualitative output of the study.

The resulting diagram (Figure 3) predicts $Co(Lac)_2(aq)$ as the dominant dissolved species across pH 1.4-8, with $Co(OH)_2(s)$ precipitation only above pH≈ 10-11, consist-

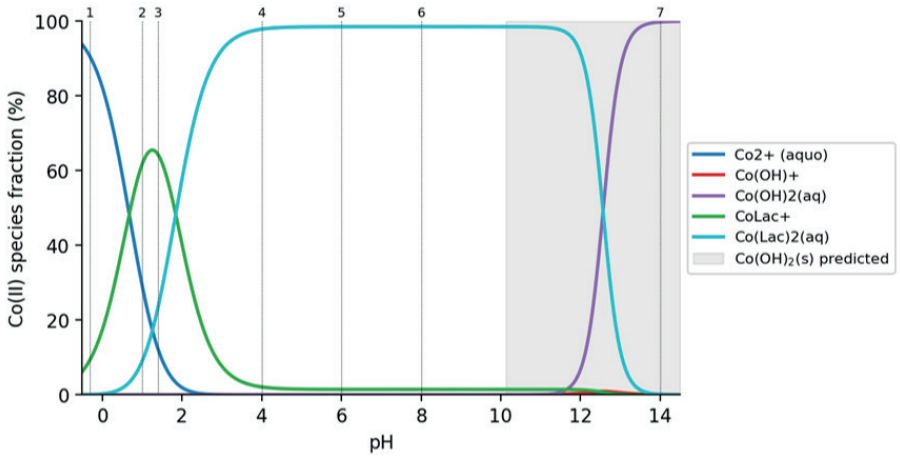


FIGURE 3: Co(II) speciation vs pH, 25°C, I≈ 3.4 M. Hydrolysis/precipitation constants: Ziemniak, Goyette & Combs (1999); Co-lactate β1/β2: NIST SRD46 via Oumarou Amadou et al. (2023), Supplementary Table S2. Ionic-strength extrapolation to I = 3.4 M (Davies-type correction) is qualitative beyond I~0.5 M; shaded band marks the region where Co(OH)2(s) precipitation is predicted.

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ent with the substantial Co dissolution observed for Experiments 3-4 (pH 1.4-4). Experimentally, however, Co dissolution yields fall to values indistinguishable from zero (below the ICP-OES limit of detection) already from pH ≈ 5 onward (Experiments 5-7), well before this calculated precipitation boundary. Since, as pointed out, the ionic-strength extrapolation used to place this boundary is itself only qualitative at I = 3.4 M, we consider it more likely that the true $Co(OH)_2$/Co-lactate solubility limit under these conditions is substantially lower than this nominal estimate, rather than that $Co(Lac)_2(aq)$ genuinely persists in solution without leaching out of the $CoWO_4$ lattice up to pH 8-10. The diagram should therefore be read as establishing the chemical plausibility of Co(II) remaining soluble as a lactate complex over part of this range, rather than as a quantitatively accurate prediction of the pH at which Co dissolution collapses.

For the Co(II)-Cl^- system specifically relevant to the HCl-only acid limit (Experiment 1), the temperature dependence of $[Co(H_2O)_6]^{2+} + 4Cl^- \rightleftharpoons [CoCl_4]^{2-} + 6H_2O$ was quantified using two independent literature ΔH°/ΔS° determinations: Zeltmann, Matwiyoff and Morgan (1968) and DeGrand, Abrams, Jenkins and Welch (2011, Table 2, activity-corrected values). At $[Cl^-]$ = 2.1 M, this calculation (Figure 4) shows the fraction of Co present as $[CoCl_4]^{2-}$ remains below 0.01% between 25 and 100 °C: bulk chloro-complexation of dissolved Co(II) therefore cannot, on its own, account for the leaching yields discussed in Section 3.3.

A comparable quantitative treatment could not be established for the W(VI) system: no literature stability constants for W(VI)-lactate complexation were identified. The persistence of dissolved tungsten in the acidic, lactate-buffered experiments (Experiments 2 and 3) is therefore discussed here as consistent with a ligand-stabilization hypothesis rather than a demonstrated mechanism: α-hydroxycarboxylates such as lactate are documented O,O-chelating ligands for other oxo-cations, and could plausibly retard the condensation/precipitation of tungstate species that otherwise occurs at low pH in a purely inorganic (HCl-only) medium. Confirming a specific W-lactate species – for example by isolating a solid analogous to the $Co(Lac)_2(H_2O)_2$ complex characterized in Oumarou Amadou et al. (2023) – is proposed as future work.

3.3 The role of inorganic acid and base addition: pH is not the only variable

The addition of HCl and NaOH used to set the pH of the leaching mixtures (Table 1) simultaneously changes the ionic-strength, the chloride or hydroxide concentration, the acid-base speciation of the lactate system, and the metal-complexation equilibria of the solution. To test directly whether the observed Co/W dissolution trends reflect pH itself or these accompanying compositional changes, additional leaching experiments were carried out in triplicate (mean ± standard deviation, n = 3 independent replicates).

Replacing HCl with HNO_3 at the same nominal acid concentration (2.1 M), for both the acid-limit condition (Experiment 1 vs. 1') and the HCl+lactate-buffer condition (Experiment 2 vs. 2'), reduced Co dissolution (6 h) from 57.99 ± 0.49% to 9.62 ± 0.75% and from 14.08 ± 0.55% to 5.31 ± 0.01%, respectively (Figure 5). W dissolution stayed at trace levels for the acid-limit pair (0.004 ± 0.001% vs. 0.007 ± 0.001%) but rose from 3.32 ± 0.17% to 8.48 ± 0.11% for the lactate-buffered pair – i.e., replacing Cl^- with NO_3^- suppresses Co dissolution in all the tested conditions while a promotion of W dissolution is observed under the lactate-buffered pair conditions. Anion identity, not only $[H^+]$, therefore controls both the extent and the selectivity of the leaching process.

Repeating selected conditions (Experiments 1, 2 and 4; Figure 6) at a common ionic-strength of 3.4 M (adjusted with $NaNO_3$) left Experiment 1 essentially unchanged (57.99 ± 0.49% → 57.57 ± 0.10% Co) but shifted Experiment 2 sharply (Co: 14.08 ± 0.55% → 3.13 ± 0.23%; W: 3.32 ± 0.17% → 8.59 ± 0.13%), while Experiment 4 – which contains no chloride – shifted only modestly (Co: 9.17 ± 0.57% → 6.84 ± 0.87%; W: 38.59 ± 1.62% → 31.17 ± 2.58%). Ionic-strength therefore affects specifically the chloride-con-

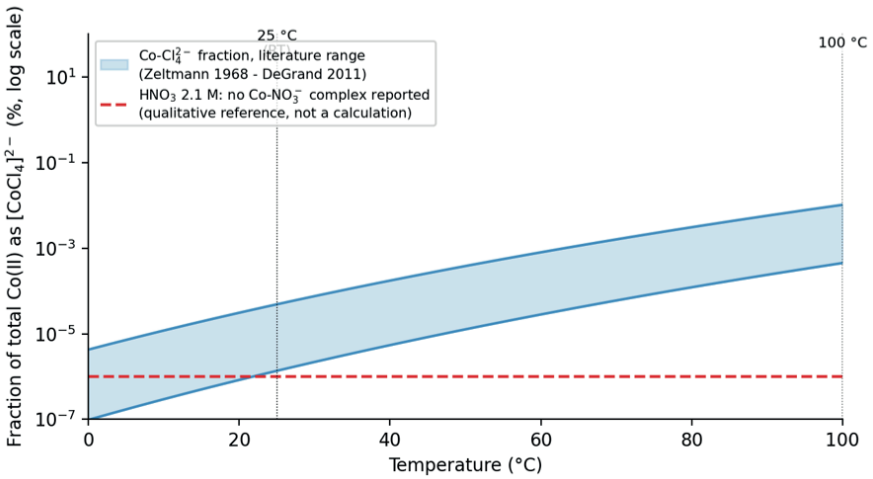


FIGURE 4: Calculated fraction of dissolved Co(II) present as [CoCl4]2- vs temperature at [Cl-] = 2.1 M (HCl 2.1 M limit), I≈ 3.4 M. Shaded band: literature range (Zeltmann, Matwiyoff & Morgan, 1968; DeGrand et al., 2011). Dashed line: qualitative reference for HNO3 (no Co-NO3- complex reported in the literature consulted).

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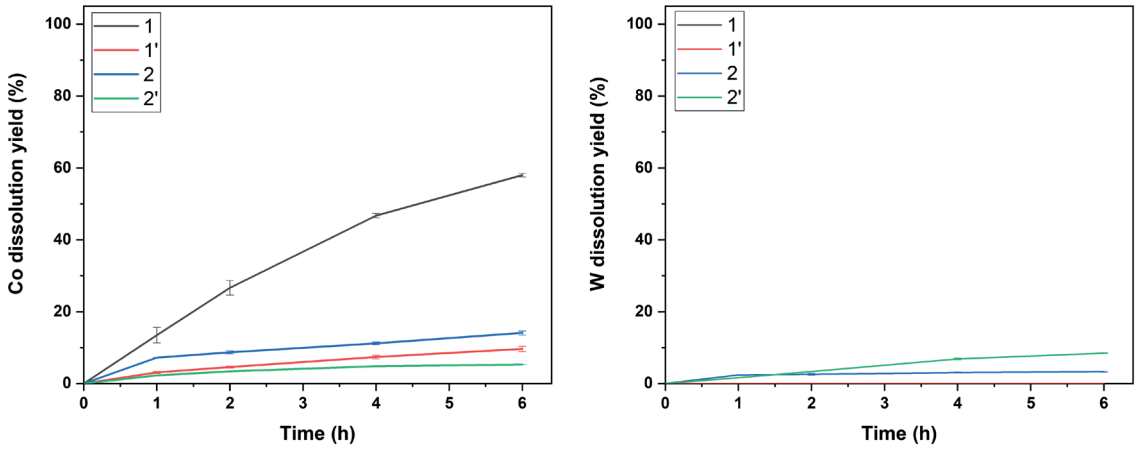


FIGURE 5: Co and W dissolution yield vs. time for HCl vs. HNO3 at matched acidity (2.1 M), acid-limit (Exp. 1/1′) and lactate-buffered (Exp. 2/2′) conditions.

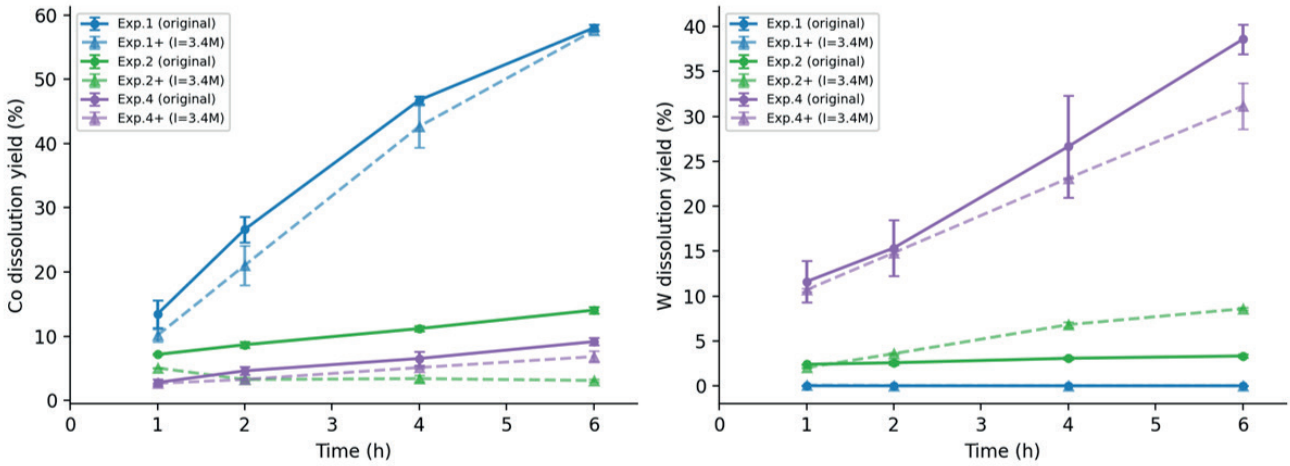


FIGURE 6: Co and W dissolution yield vs. time, original protocol vs. fixed ionic-strength (I = 3.4 M, NaNO3-adjusted), for Experiments 1, 2 and 4.

taining condition, not the chloride-free lactate buffer alone, indicating that the effect is not a generic medium artifact but is coupled to the presence of Cl^-.

A mass-action estimate of Co(II)-Cl^- speciation (Section 3.2, Figure 4), based on independent literature ΔH°/ΔS° values, indicates that at [Cl^-] = 2.1 M the $[CoCl_4]^{2-}$ fraction remains below 0.01% even at 100 °C. The magnitude of the experimental Cl^-/NO_3^- effect on Co dissolution is therefore too large to be explained by a shift in bulk aqueous speciation, and more plausibly reflects a chloride-mediated effect at the $CoWO_4$ solid-liquid interface (e.g., surface complexation facilitating Co release from the lattice) rather than a change in the stability of already-dissolved Co(II). This interfacial hypothesis is offered as a plausible chemical rationale, not a proven mechanism; the experimental comparisons above are the primary evidence that pH alone does not control the observed Co/W selectivity.

4. CONCLUSIONS

Combined thermal–chemical treatment of HM-waste represents an effective and tunable strategy for the recovery of tungsten and cobalt. The systematic investigation of $WO_3/CoWO_4$ oxidized powders in lactic acid solutions at different pH values clearly highlights the strong pH dependence of metal dissolution and the key role of chemical speciation in governing selectivity. As expected, $CoWO_4$ shows enhanced dissolution under acidic conditions, whereas WO_3 is preferentially solubilized at near-neutral to mildly alkaline pH. Under extreme conditions, this opposite behavior becomes particularly evident: maximum Co dissolution (57.99%) was obtained at pH lower than 1 with negligible W solubilization (close to 0%), while at pH 14 W dissolution was quantitative with almost no Co leaching. These findings confirm that, for practical application, pH control is a powerful lever to modulate the W/Co leaching ratio and, consequently, process selectivity. However, a Co(II) speciation model built from independent literature thermodynamic data, together with dedicated experiments comparing HCl and HNO_3 at matched acidity and at fixed ionic-strength, showed that pH is not the only variable at play: the identity of the acid counter-ion (Cl^- vs. NO_4^-) and the ionic-strength of the medium independent-

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ly and significantly affect Co dissolution, most plausibly through a chloride-mediated effect at the $CoWO_4$ solid-liquid interface rather than through a shift in bulk aqueous speciation (Sections 3.2-3.3). Beyond simple pH effects, the HLac/Lac^- conjugate system plays a decisive role in expanding the solubility window of both metals through complex formation. Importantly, these results demonstrate that bio-derived and biodegradable carboxylate systems can effectively replace conventional strong alkaline leaching agents. Comparable tungsten dissolution efficiencies and selectivity were achieved at mild conditions (pH ≈ 6) as compared to highly alkaline systems (pH ≈ 14), significantly improving the environmental compatibility and safety of the process. Complete selectivity toward cobalt from oxidized powders (POX) in the presence of HLac remains instead challenging. However, when considering the different chemical forms encountered along the ORC process (WO_3/$CoWO_4$ in POX, W/Co in REW, and WC/Co in OXR), the HLac/Lac^- buffer system proved highly effective in selectively dissolving cobalt from WC/Co powders.

Overall, this work provides insight into the reactivity and practical guidelines for designing a smart, selective, and sustainable recycling route for HM waste. The ability to tailor W and Co recovery through mild, bio-based leaching systems represents a significant step toward more circular and environmentally responsible management of critical raw materials. Translating these leaching results into a complete closed-loop process will additionally require efficient downstream separation and recovery of the dissolved Co and W from the pregnant leach liquors, for which established techniques such as solvent extraction, ion exchange, and electrowinning provide well-documented routes (Song et al., 2018; Karmaker et al., 2022; Karmakar et al., 2018).

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