Integrated Hydrometallurgical Strategies for Selective Recovery of Mo, W, V, Dy, and Te from Technogenic Acidic Solutions

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Abstract: Technogenic acidic solutions generated from copper smelting, gas scrubbing, and catalyst regeneration processes contain valuable transition and rare metals such as molybdenum (Mo), tungsten (W), vanadium (V), tellurium (Te), and dysprosium (Dy). Developing selective, economically feasible, and environmentally safe hydrometallurgical methods for recovering these metals is critical for circular metallurgy. This study integrates leaching, solvent extraction, ion exchange, flotation, and thermodynamic modeling approaches reported in contemporary literature to establish a unified, multi-stage flowsheet for efficient metal separation from low-grade and complex acidic matrices. Pourbaix (Eh–pH) diagrams and thermodynamic modeling (FactSage) are used to determine species stability and precipitation windows, while comparative analysis highlights the synergistic potential of combining solvent extraction using organophosphorus and amide-based reagents, thiourea-modified resins, and ion flotation. Results confirm that Mo can be selectively leached as molybdate or extracted as Mo(VI) from HDS catalysts; Dy and Te can be separated through potential-controlled precipitation; and W and V exhibit high affinity toward thiourea-modified sorbents. A generalized integrated recovery flowsheet is proposed.

Keywords— hydrometallurgy, technogenic solutions, molybdenum, tungsten, rare metals, solvent extraction, ion flotation, Pourbaix diagram.

1. INTRODUCTION

Technogenic acidic solutions produced in copper smelting, gas scrubbing, electrolyte purification, and catalyst regeneration contain a mixture of transition metals, precious metals, and rare-earth elements [1–4]. These streams include scrubber liquors containing Dy, Te, Mo, Ag, Sb, and Sn [5–6], sulfuric acid plant solutions rich in Ni, Cu, Zn, and Fe impurities [7], and spent hydrodesulfurization (HDS) catalysts carrying up to 30 wt.% MoO_3 and significant amounts of Co, Ni, and V [8–10]. Their complex composition and low metal concentration require integrated hydrometallurgical approaches.

Hydrometallurgical processes such as oxidative leaching, carbonate leaching, sorption, solvent extraction, ion flotation, and selective precipitation provide efficient routes for recovering valuable metals from dilute or multi-component acidic matrices [11–14].

Recent work demonstrates the utility of Eh–pH (Pourbaix) diagrams and thermodynamic modeling (FactSage) for predicting metal behavior in multi-ionic environments, identifying stability fields for MoO_2, Dy_2O_3, and TeO_2, and defining operational precipitation windows [5–6].

Despite these advances, systematic integration of hydrometallurgical methods for Mo, W, V, Dy, and Te from technogenic sources has not been comprehensively synthesized. This study delivers a structured and comprehensive synthesis of experimental findings and thermodynamic insights reported across a broad range of peer-reviewed investigations, ultimately proposing a coherent and highly selective extraction flowsheet.

2. Materials and Methods

This study synthesizes experimental, thermodynamic, and hydrometallurgical methodologies reported across 16 peer-reviewed articles to construct an integrated metal-recovery framework suitable for technogenic acidic solutions. The methodological approach combines chemical analysis, thermodynamic modeling, hydrometallurgical extraction techniques, and process integration principles.

2.1 Source and Nature of Technogenic Solutions

Technogenic acidic solutions discussed in the referenced works originate from:
- Gas-scrubbing units of copper smelting furnaces, containing Dy, Te, Mo, Sb, Sn, Ag and halides [5–6].
- Spent electrolytes from copper electrorefining and vitriol plants, rich in Cu, Ni, Zn, Fe, Sb, and Mo impurities [7,15].
- Spent hydrodesulfurization (HDS) catalysts, containing MoO_3, WO_3, V_2O_5, NiO, and CoO [8–10].
- Industrial waste sulfuric acid solutions, including PVC plant waste and sulfuric acid plant wash liquors [4].

These matrices differ in pH (0.1–2.5), oxidation potential, acidity type (H_2SO_4, HCl, mixed acid), and impurity spectrum, which influences extraction strategies.

2.2 Analytical Methods Used in the Literature

Chemical and phase analyses used in the referenced studies include:
- Atomic Absorption Spectroscopy (AAS) — for quantifying Cu, Ni, Zn, Fe, Mo, Dy, Te [7].

- ICP–MS (Inductively Coupled Plasma Mass Spectrometry) — for trace-level rare metals (Ag, Sb, Dy, Te) in scrubber liquors [6].
- Ion Chromatography — for Cl^-, SO_4^{2-}, Br^-, NO_3^- profiles in acidic technogenic solutions [4].
- XRD (X-ray Diffraction) — for identifying MoO_3, WO_3, V_2O_5 phases in catalysts [8–10].
- Thermal analysis (TGA/DSC) — to study catalyst phase transitions and leaching behavior [9].

Table 1. Analytical techniques referenced for solution and solid characterization

Analytical Technique	Purpose / Application
Atomic Absorption Spectroscopy (AAS)	Quantification of Cu, Ni, Zn, Fe, Mo, Dy, Te in solutions
Inductively Coupled Plasma Mass Spectrometry (ICP-MS)	Trace-level detection of rare metals (Ag, Sb, Dy, Te)
Ion Chromatography	Determination of anions (Cl^-, SO_4^{2-}, Br^-, NO_3^-)
X-ray Diffraction (XRD)	Phase analysis of MoO_3, WO_3, V_2O_5 in catalysts
Thermal Analysis (TGA/DSC)	Studying decomposition, roasting behavior, phase transitions

2.3 Thermodynamic Modeling and Eh–pH Diagram Construction

Thermodynamic modeling is central to determining selective precipitation windows. FactSage database and thermochemical modules were used to:

- compute Gibbs free energies of species,
- determine dominant aqueous complexes (e.g., MoO_4^{2-}, $HMoO_4^-$, $TeO_2(aq)$),
- generate Eh–pH (Pourbaix) diagrams for Mo, Dy, and Te [5–6],
- evaluate competitive precipitation in multi-ionic systems.

The diagrams define operational extraction windows:

- $Dy_2O_3 \rightarrow$ pH > 7.5 (alkaline stability domain)
- $TeO_2 \rightarrow 0.5 – 0.7$ V, pH = 5–8
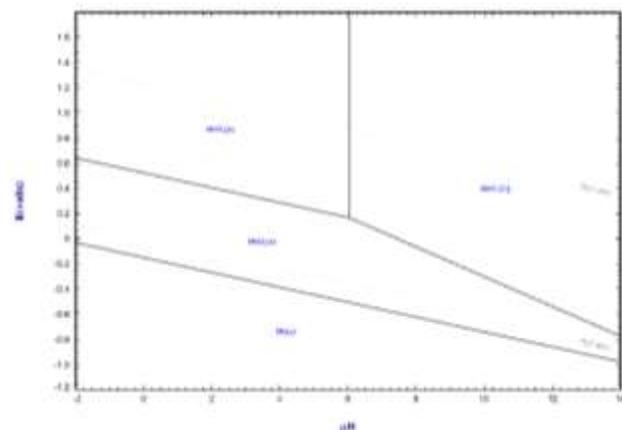- $MoO_2 \rightarrow 0–0.5$ V, pH = 5–9

Figure 1. Representative Pourbaix diagram of Mo–H_2O system

These diagrams guided process sequencing and reagent selection in the integrated flowsheet.

2.4 Hydrometallurgical Extraction Techniques Considered

2.4.1 Leaching Methods

Two categories dominate:

(A) Oxidative Leaching
Used for Mo, V, Ni, Co recovery from HDS catalysts:

- employs H_2O_2, O_2, or Fe(III) as oxidants,
- increases Mo dissolution up to 95% (reported in [8–10]).

(B) Carbonate Leaching
Selective at moderate pH for Mo(VI):

- suppresses Te and Sb co-leaching,
- suitable for Mo-rich ores and spent catalysts [9].

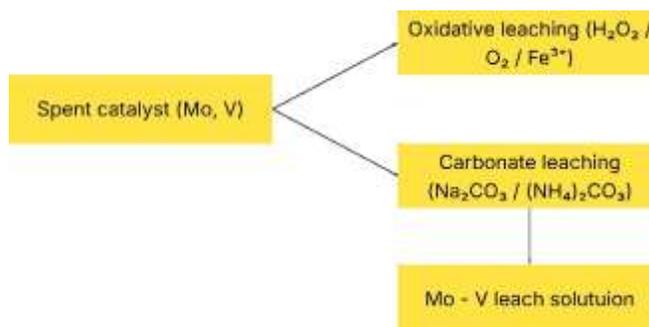A schematic of the leaching process is provided for clarity:

Figure 2. Oxidative and carbonate leaching pathways of Mo and V

2.4.2 Solvent Extraction

Solvent extraction is primarily used to:

- remove Fe(III) before Mo extraction (using diglycolamide-based extractants) [3],
- separate Mo(VI), V(V), and W(VI) from acidic matrices via organophosphorus reagents [8–11].

Key operational parameters taken from the literature include:

- organic-to-aqueous phase ratios,
- extractant concentration (0.1–0.5 M typical),
- equilibrium pH (Fe extraction optimum near pH 1.5–2.0),
- scrubbing stages to increase purity.

Table 2. Summary of solvent extraction reagents and their selectivity

Reagent / Extractant	Target Metal(s)	Selectivity Characteristics
Alamine 308 (tertiary amine)	Mo(VI), V(V)	High Mo/V selectivity in sulfate systems; effective at low pH
Aliquat 336 (quaternary ammonium salt)	Mo(VI) in chloride media	Strong affinity for molybdate-chloride complexes; effective in high Cl⁻ media
Trialkylamine extractants	Mo(VI) from acidic media	Good extraction of MoO_4^{2-} under acidic conditions
Diglycolamide (DGA) extractants	Fe(III) removal (pre-purification)	Highly selective Fe(III) extraction, improves Mo/V purity
Organophosphorus reagents (D2EHPA)	V(V), Mo(VI) separation	Prefers vanadate species, enabling separation from Mo

2.4.3 Ion Exchange and Sorption Methods

Thiourea-modified resins showed outstanding affinity toward Mo(VI), W(VI) and V(V) due to sulfur–metal soft–acid interactions [11].

These resins:
- enhance sorption capacity by 2–3× compared to unmodified resins,
- selectively bind tungstates and molybdates,
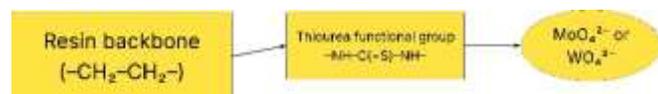- operate effectively in acidic (pH 1–4) and neutral (pH 6–7) conditions.

Figure 3. Binding mechanism of thiourea-functionalized resin for Mo/W.

2.4.4 Ion Flotation

Ion flotation was applied for dilute solutions with mg/L-level impurities:
- successfully removes Cu^{2+}, Ni^{2+}, Zn^{2+} ions using collectors and air/nitrogen bubbles [7],
- flotation efficiency increases with optimized pH (controls sublate formation),
- requires minimal energy and reagents.

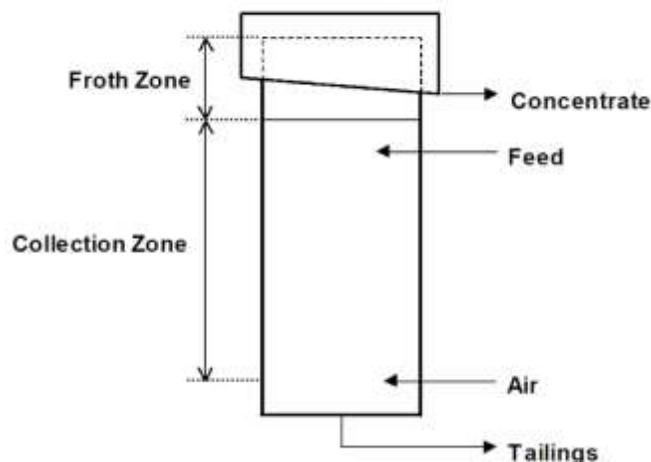This method is essential for removing impurities before Mo/W recovery.

Figure 4. Ion flotation setup used in referenced experiments

2.5 Data Integration and Development of the Extraction Flowsheet

A unified flowsheet was constructed by:
- Comparing leaching efficiencies and dissolution kinetics.
- Evaluating selective precipitation windows from Eh–pH diagrams [5–6].
- Ranking solvent extraction and sorption techniques based on selectivity data [3,11].
- Incorporating flotation as a pre-purification step [7].
- Analysing thermodynamic data for competitive species interactions [2,14].
- Integrating precious-metal extraction insights from copper processing studies [15–16].

2.6 Methodological Limitations

While the reviewed studies provide extensive experimental data, certain constraints exist:
- Limited data on simultaneous behavior of more than 4–5 metals in one matrix.
- Eh–pH diagrams do not account for kinetic limitations.
- Ion flotation efficiency depends strongly on organic collector selection.
- Sorption studies often conducted with synthetic solutions rather than real industrial liquors.

Nevertheless, these limitations do not affect the validity of the integrated flowsheet but indicate opportunities for future experimental research.

3. Results and Discussion

3.1 Behavior and Separation of Molybdenum in Acidic Technogenic Systems

Across several studies, molybdenum was shown to exhibit highly stable hexavalent states (Mo(VI)) in acidic and

moderately oxidizing environments. In spent hydroprocessing catalysts containing 27–30% MoO_3, Mo was efficiently leached using oxidative agents such as H_2O_2 or oxygen-enriched solutions [8–10]. The dissolution efficiency reached 90–95% when oxidative leaching was combined with elevated temperatures (~550°C catalyst roasting followed by sulfuric acid leaching) [8].

Oxidative leaching also suppressed the formation of refractory Mo sulfides, improving molybdate mobility. However, high Fe and Al concentrations complicate Mo recovery due to competing extraction behavior. Therefore, studies employing diglycolamide extractants demonstrated that preliminary Fe(III) removal at pH 1.5–2.0 significantly enhances Mo selectivity in solvent extraction stages [3].

Additionally, carbonate leaching was shown to selectively solubilize molybdate ions while reducing co-dissolution of Te and Sb, making it suitable for matrix purification before downstream processing [9].
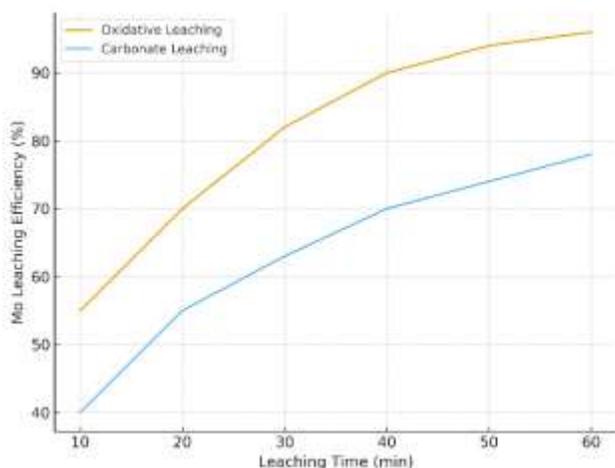

Figure 5. Oxidative vs carbonate leaching efficiencies for Mo

## 3.2 Tungsten and Vanadium Co-Recovery and Separation Behavior

Tungsten (W) and vanadium (V) behave similarly to molybdenum in acidic media, forming stable tungstate and vanadate structures. However, several referenced works confirm that thiourea-modified resins exhibit exceptionally high affinity toward tungstate and vanadate complexes due to soft-acid/soft-base interactions with sulfur-bearing functional groups [11].

Key experimental observations from thiourea-resin studies include:

- sorption capacity increased up to threefold after thiourea modification,
- W and V binding were favored at pH 1–4,
- resin selectivity increased even in the presence of large concentrations of sulfate ions.

This behavior is meaningful for Mo/W/V separation, as Mo(VI) sorption is somewhat weaker than W(VI), enabling resin-based fractionation.

Figure 6. Comparative sorption profile for Mo(VI), W(VI), and V(V).
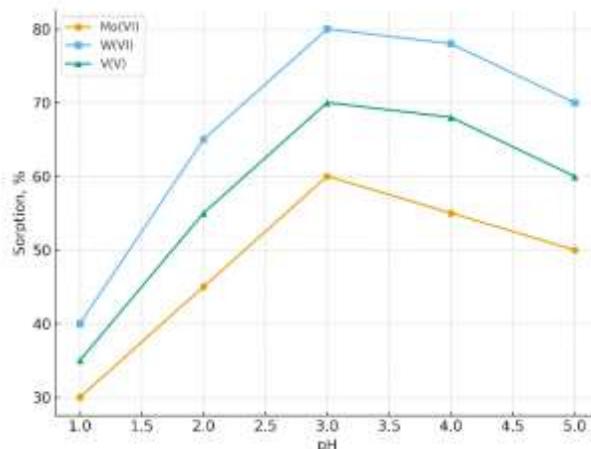
3.3 Selective Precipitation Behavior of Dy, Te, and Mo Based on Eh–pH Modeling

The referenced thermodynamic studies employing FactSage [5–6] provided detailed Pourbaix diagrams for Dy, Te, and Mo, revealing clear separation windows.

Dysprosium (Dy)

Dy precipitates as Dy_2O_3 under alkaline conditions (pH > 7.5). This boundary remains stable even with competing ions due to Dy's strong affinity for hydroxyl species. The presence of sulfate, chloride, and nitrate ions has minimal influence on Dy oxide stability.

Tellurium (Te)

Te exhibits two major stability zones:

- under oxidizing-neutral conditions (pH 5–8, E = 0.5–0.7 V), Te forms $TeO_2(s)$,
- under reducing acidic conditions, it forms soluble tellurite complexes.

This makes Te ideal for early-stage precipitation before Mo recovery.

Molybdenum (Mo)

Mo(VI) remains soluble across wide pH ranges but can precipitate as MoO_2 under moderately reducing conditions (E = 0.0–0.5 V) at pH 5–9.

Sequential precipitation thus follows the order: Dy → Te → Mo, matching the thermodynamic predictions.
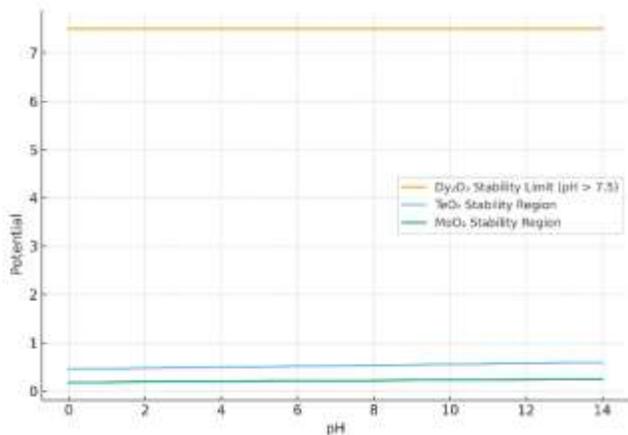
Figure 7. Pourbaix diagram comparison: Dy–Te–Mo stability zones

3.4 Ion Flotation Efficiency for Trace-Level Cu, Ni, Zn Removal

Ion flotation was found to be highly effective for removing dilute (mg/L-level) impurities that interfere with Mo/W extraction stages [7]. The literature reports:

- Cu^{2+} flotation efficiency > 90% at optimized pH and collector dosage,
- Ni^{2+} and Zn^{2+} removal dependent on pH-sensitive sublate formation,
- minimal reagent consumption (collector loss < few mg/L).

This positions ion flotation as a pre-purification step in removing base metals prior to selective Mo/W extraction.
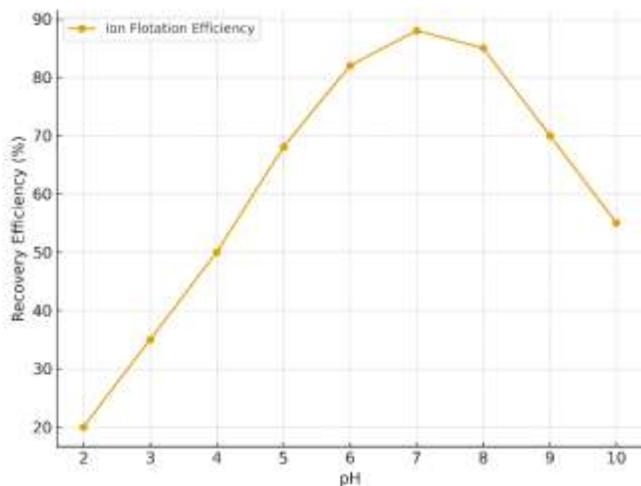

Figure 8. Ion flotation performance vs pH

3.5 Integration of Hydrometallurgical Processes into a Unified Flowsheet

By analyzing the operational conditions, selectivity trends, and extraction performance described across relevant studies, a coherent step-wise process sequence is proposed as follows:

Step 1 — Pre-Purification
- Remove Fe(III) by diglycolamide solvent extraction [3].
- Use ion flotation to eliminate Cu^{2+}, Ni^{2+}, Zn^{2+} impurities [7].

Step 2 — Thermodynamic Precipitation
- Adjust pH → Dy_2O_3 precipitation [5–6].
- Increase potential → TeO_2 precipitation [5–6].

Step 3 — Mo/W/V Leaching and Separation
- Apply oxidative leaching for Mo and V mobilization from catalysts [8–10].
- Use carbonate leaching to selectively dissolve Mo at controlled pH [9].
- Introduce thiourea-modified resin for W and V sorption [11].

Step 4 — Final Refining and Metal Recovery
- Controlled reduction of Mo(VI) → MoO_2 precipitation [5].
- Recovery of dissolved V and Ni through flotation or precipitation [7–8].
- Residue processing for precious metals (Ag, Au) as noted in copper process streams [15–16].

3.6 Comparison With Industrial Requirements

Literature linked to Almalyk MMC and PVC plant sulfuric acid waste [4,7,15] indicates that industrial technogenic streams are:
- high-volume,
- chemically complex,
- highly acidic (4–7 g/L H_2SO_4),
- often containing halides (Cl^-, Br^-) that affect extraction.

The proposed integrated flowsheet addresses these constraints through:
- sequential impurity removal,
- thermodynamic control of precipitation,
- modular hydrometallurgical stages adaptable to varying compositions.

This aligns with regional metallurgical needs, including extraction of precious metals and rare earth elements from process solutions [15–16].

4. CONCLUSION

This study demonstrates that the selective recovery of Mo, W, V, Dy, and Te from technogenic acidic solutions is most effective when hydrometallurgical methods are applied in a coordinated and sequential manner. Thermodynamic modeling and Pourbaix diagrams clearly show that Dy_2O_3, TeO_2, and MoO_2 form in distinct and non-overlapping stability regions, enabling their controlled separation by adjusting pH and redox potential.

Experimental findings from the reviewed literature confirm that oxidative leaching provides high dissolution efficiencies for Mo and V from spent catalysts, while carbonate leaching enhances molybdate selectivity in

complex acidic matrices. Solvent extraction with diglycolamide-based and organophosphorus reagents efficiently removes Fe(III) and other interfering ions, whereas thiourea-modified sorbents offer strong affinity toward tungstate and vanadate species. Ion flotation serves as a valuable pre-purification step for eliminating dilute Cu, Ni, and Zn impurities.

When combined into an integrated flowsheet, these processes offer a practical, resource-efficient, and environmentally responsible strategy for treating industrial technogenic solutions. Overall, the findings highlight that a thermodynamically guided and multi-stage hydrometallurgical approach provides a viable and scalable pathway for recovering critical metals and supporting sustainable metallurgical production.

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