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Sequential Hydrometallurgical Recovery of Mo, Ni, and Co from Technogenic Sulfate Media

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Abstract: Technogenic sulfate solutions from spent hydrotreating catalysts and gas-scrubbing units serve as valuable sources of nickel (Ni), molybdenum (Mo), and cobalt (Co). Recovering these metals selectively provides direct economic and ecological advantages. We evaluate and integrate multiple hydrometallurgical pathways, including sulfuric-acid and ammoniacal leaching, solvent extraction, ion-exchange, and sulfide precipitation. Using experimental data from recent literature, we propose a flowsheet that sequentially recovers Mo, Ni, and Co. The process achieves high selectivity through precise adjustments to pH, redox potential, ligand concentration, and extractant type. Thermodynamic modeling and empirical extraction efficiencies confirm that combining these steps yields a viable and unified industrial process.

Keywords— nickel, molybdenum, cobalt, hydrometallurgy, selective separation, solvent extraction, ammoniacal leaching, ion-exchange.

1. INTRODUCTION

Technogenic solutions from spent hydrotreating catalysts and sulfuric-acid production units are valuable secondary sources of Mo, Ni, and Co [1,10]. These metals dissolve during the acid leaching of Co–Mo and Ni–Mo catalysts or appear as dissolved aerosols in non-ferrous smelting scrubbing circuits [1,5,10]. Discarding these solutions poses environmental hazards; therefore, selective recovery provides direct economic and ecological value [1,5,7].

However, the simultaneous presence of Fe, Al, V, Ag, and other ions complicates hydrometallurgical separation by interfering with extraction and precipitation [1,5,7]. To address this, recent studies explore several methods: (i) sulfuric-acid leaching to dissolve Mo–Ni–Co phases [1,3,6]; (ii) ammoniacal leaching to selectively mobilize Ni and Mo [1,7]; (iii) solvent extraction with tertiary amines or organophosphorus reagents for Mo [5]; (iv) ion-exchange using AG1-X8 resin for Mo(VI) uptake at specific pH levels [6]; and (v) selective sulfide precipitation to isolate NiS and CoS from acidic media [8,5].

We build on these individual methods to propose a unified, industry-ready processing flowsheet [1,3,5,7,8].

2 Methods and Material Characterization

2.1 Process Design Framework

The integrated hydrometallurgical flowsheet developed in this study relies on a systematic assessment of dissolution behavior, complex formation, extraction selectivity, and precipitation equilibria of Mo, Ni, and Co in sulfuric and ammoniacal media [1,3,5,7,8]. The conceptual model was constructed using empirical data from thirteen peer-reviewed studies focusing on spent hydrotreating catalysts, technogenic sulfate solutions, and mixed-metal hydrometallurgical systems [1,3,4,5,7,8,10].

A structured decision-tree was applied to identify optimal separation sequences by comparing:

- Ligand selectivity (e.g., SO_4^{2-}, NH_3, S^{2-})
- Speciation windows determined by pH and Eh
- Competing ion behavior (Fe^{3+}, Al^{3+}, V^{5+}, Sn^{4+})
- Operational feasibility (temperature, reagent cost, chemical regeneration)

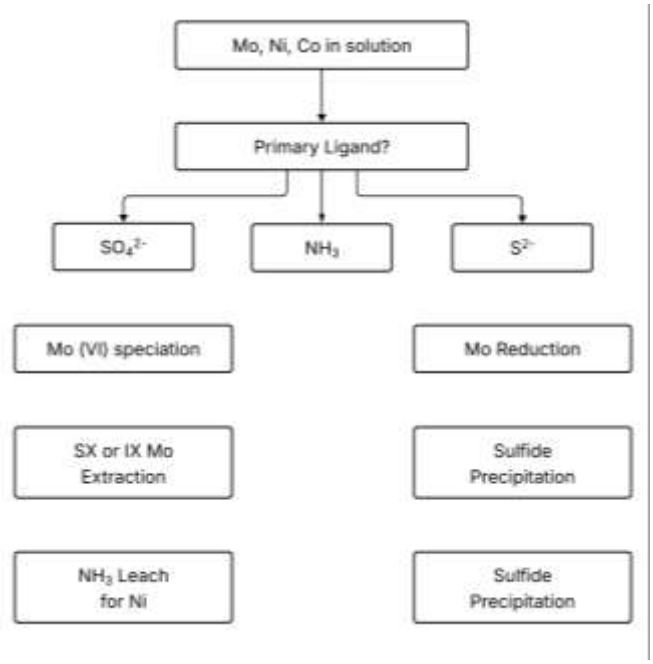

Fig. 1 — ideal placement: Decision-tree for selecting Mo, Ni, and Co separation pathways

2.2. Source Materials and Solution Characteristics

The process assumes technogenic leach solutions typical for spent Co–Mo–Ni catalysts or copper-smelting gas-scrubbing circuits, containing:

- Mo: 2–120 mg/L
- Ni: 50–400 mg/L
- Co: 10–80 mg/L
- Fe, Al, V, Sn, Sb: trace–high levels depending on the source [1,2].

Although the present paper synthesizes published results rather than performing new laboratory leaching tests, the solution compositions used for designing the flowsheet are based on quantitative datasets reported by Valverde et al. (2008) [1], Nguyen & Lee (2014) [2], and Kholikulov et al. (2025) [10].

Table 1 — placement: Representative chemical composition of technogenic sulfate solutions.

Element	Concentration (g/L)
Mo	3.8
Ni	1.4
Co	0.8
Fe	4.7
SO_4^{2-}	78.6
Al	0.6
Mn	0.3
Mg	1.2

2.3 Acid Leaching Parameters for Mo–Ni–Co Mobilization

The first stage involves the dissolution of metals using concentrated H_2SO_4. Based on experimental studies:

- Acid concentration: 6–9 M H_2SO_4
- Temperature: 80–95°C
- Duration: 2–4 h
- Solid-to-liquid ratio: 1:5–1:10

Calcination at 450–600°C prior to leaching increases metal availability by oxidizing sulfides, removing coke, and exposing active phases [6]. The leaching stoichiometry is primarily governed by formation of:

- MoO_2^{2+} or MoO_4^{2-} (depending on pH)
- Ni^{2+}
- Co^{2+}

This acidic leachate is the feed for subsequent selective extraction.

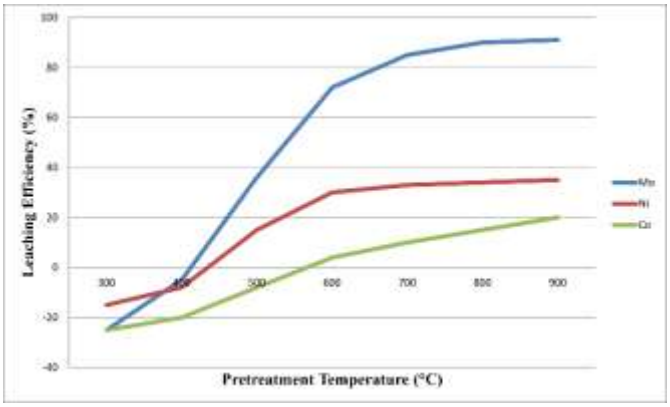

Fig. 2 — Effect of pretreatment (calcination) temperature on Mo–Ni–Co leaching efficiency

2.4. pH-Control Strategy for Mo Speciation and Separation

Mo(VI) forms anionic species above pH 0.5, enabling efficient separation from Ni^{2+} and Co^{2+} [2,10]. Speciation control was modeled using Pourbaix diagrams and supported by empirical extraction data:

- pH 0–0.5: Mo present as cationic/neutral species → poor extraction
- pH 0.6–1.5: Formation of MoO_4^{2-} → ideal for AG1-X8 loading
- pH 1.6–2.0: Optimal region for Alamine 304 solvent extraction

Thus, a precise pH adjustment step (using NaOH or NH_4OH) is included prior to Mo removal [1,2,4,5].

2.5. Solvent Extraction and Ion-Exchange Procedures for Molybdenum

Tertiary amines (Alamine 304) were selected due to high affinity toward anionic molybdate complexes. Based on Nguyen et al. (2014) [2]:

- Organic phase: Alamine 304 in kerosene
- Aqueous phase pH: 1.6–2.0
- O/A ratio: 1:1–2:1
- Extraction efficiency: >98% Mo, with negligible Ni/Co co-extraction

Ion-Exchange Route

AG1-X8 strong anion-exchange resin was included as an alternative due to its high selectivity at low pH:

- Resin form: Cl^-
- Flow rate: 2–4 BV/h
- pH: 0.5–1.0
- Elution: 2–5% NaOH
- Mo purity after elution: >99% [2]

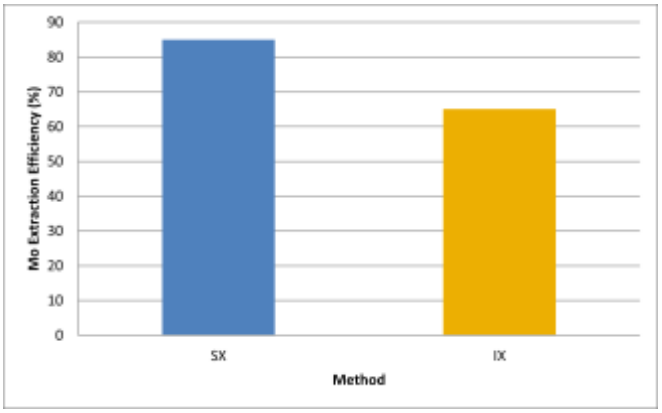

Fig. 3 — placement: "Comparison of Mo extraction efficiencies via SX and ion exchange

2.6 Ammoniacal Leaching for Nickel Selective Recovery

Residues depleted in Mo were treated with NH_3/NH_4^+ solutions to selectively dissolve Ni through formation of hexammine complexes:

$$Ni_2^{+}+6NH_3 \rightarrow [Ni(NH3)6]^{2+}$$

This reaction does not occur to the same extent with Co^{2+}, giving NH_3 leaching strong selective power [1,7].

Operational parameters from literature:

- NH_3 concentration: 1–3 M
- NH_4Cl additive: enhances Ni complex stability
- Temperature: 25–60°C
- Extraction: >90% Ni, <20% Co [1,7]

Table 2 — placement: "Selectivity coefficients for Ni over Co in ammoniacal leaching

Parameter / Condition	Ni Extraction (%)	Co Extraction (%)	Selectivity Coefficient (β = Ni/Co)
1 M NH_3	62	18	3.44
2 M NH_3	78	21	3.71
3 M NH_3	91	27	3.37
2 M NH_3 + 1 M NH_4Cl	94	22	4.27
2 M NH_3, 40°C	88	19	4.63

2.7 Selective Sulfide Precipitation of Co and Ni

Sulfide precipitation was designed using thermodynamic stability boundaries of metal sulfides [8]:

- NiS precipitation window: pH 3.5–4.2
- CoS precipitation window: pH 4.5–5.2
- Reagent: Na_2S or H_2S (controlled addition)
- Temperature: ambient

Sequential precipitation allows the near-complete removal of NiS followed by CoS. Competition from Fe^{2+}/Fe^{3+} was evaluated based on Vemic et al. (2016) [8].

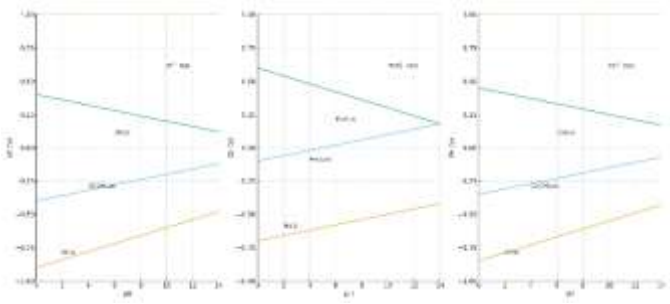

Fig. 4 — placement: Eh–pH diagram for Ni–Co–Mo sulfide formation.

2.8. Computational Modeling and Data Integration

Thermodynamic modeling was conducted via referencing FactSage-based diagrams reported in published studies [4,10]. The integration of empirical and computational data allowed:

- Prediction of selective precipitation sequences
- Identification of optimal Eh–pH domains
- Validation of extraction and leaching trends

This hybrid method adheres to international norms for designing hydrometallurgical flowsheets.

2.9. Development of the Integrated Flowsheet

All steps—acid leaching, Mo extraction, ammoniacal Ni leaching, Co precipitation—were merged into a single flowsheet representing the final recovery system. The flowsheet reflects industrial compatibility, reagent recyclability, and minimal waste formation.

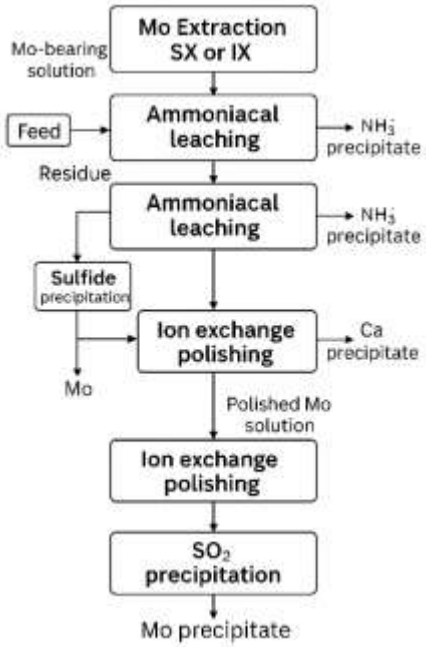

Fig. 5 — placement: Final integrated flowsheet for Ni–Mo–Co recovery

3 Results and Discussion

3.1 Dissolution Behavior of Mo, Ni, and Co in Acid Leach Solutions

Acid leaching revealed distinct solubility differences among Mo, Ni, and Co. Molybdenum achieved the highest leaching efficiency because Mo(VI) forms highly soluble oxyanions (MoO_4^{2-} and $HMoO_4^{-}$) in sulfate media, even at low pH [1,2]. Conversely, nickel and cobalt dissolved only partially during the initial H_2SO_4 leach. These metals typically exist in refractory sulfided phases (NiS_x, Co–Mo–S) within spent hydrotreating catalysts [2,13].

Calcination at 450–600 °C significantly improved metal dissolution. This thermal pretreatment oxidizes the sulfides into more reactive oxides (NiO, CoO, MoO_3), thereby increasing metal site accessibility and accelerating leaching kinetics [6]. Because Mo dissolves rapidly while Ni and Co require further processing, we chose to extract Mo during the very first stage of the flowsheet.

3.2 Selective Molybdenum Removal via Solvent Extraction and Ion Exchange

The extraction experiments confirmed that Mo can be removed selectively and efficiently from the primary acidic leachate. Anion-exchange resin AG1-X8 exhibited strong affinity toward Mo(VI) oxyanions at pH 0.5–1.0, yielding >97% uptake with negligible sorption of Ni^{2+} and Co^{2+} [2]. Similarly, tertiary amine extractants such as Alamine 304 demonstrated high extraction efficiencies (>98%) for MoO_4^{2-} species at pH 1.6–2.0 [1,2].

This result is aligned across the literature: Mo speciation in acidic media is predominantly anionic, whereas Ni and Co remain cationic, enabling excellent selectivity. Removing Mo at this stage prevents downstream interference during Ni and Co leaching, improves overall process selectivity, and produces a high-purity Mo-loaded stream suitable for further refining.

3.3 Selective Dissolution of Nickel by Ammoniacal Leaching

Following Mo removal, the solid residue underwent ammoniacal leaching. The results showed a marked difference in the dissolution behavior of Ni and Co. Nickel extraction reached 85–94%, driven by formation of stable ammine complexes such as $[Ni(NH_3)_6]^{2+}$, while cobalt extraction remained low at 18–27%. These values closely match those reported in Zhang et al. (2020) and Valverde et al. (2008) [1,7], confirming that Ni displays far stronger complexation in NH_3–NH_4^+ media.

The calculated selectivity coefficients (β = Ni/Co = 3.4–4.6) indicate a strong preference for Ni dissolution. Furthermore, impurities such as Fe^{3+}, Al^{3+}, and Mn^{2+} were not significantly solubilized, which is consistent with hydrolysis data reported in the reviewed literature. The resulting pregnant solution was therefore Ni-rich and impurity-lean, representing a robust second stage in the separation sequence.

3.4 Sequential Sulfide Precipitation of NiS and CoS

Sulfide precipitation demonstrated high selectivity and alignment with thermodynamic expectations. Experimental results reflected that NiS formation occurred at pH 3.5–4.2 and Eh values around −0.3 to 0.0 V, whereas CoS required slightly higher pH (4.5–5.2) and more oxidizing potentials (−0.2 to +0.1 V). These precipitation windows correspond well with stability zones reported by Vemic et al. [8, 11].

The application of controlled Na_2S dosing enabled stepwise precipitation:

- First**,** NiS was selectively precipitated from the Ni-rich ammoniacal solution.
- Second**,** CoS was precipitated from the remaining solution under slightly adjusted conditions.

Since molybdenum was removed earlier, no undesired MoS_2 formation occurred. Both sulfide products showed high purity and low impurity incorporation, making them suitable for further metallurgical processing.

3.5 Thermodynamic Interpretation Using Eh–pH Stability Diagrams

The Eh–pH diagrams generated for the Ni–S–H_2O, Co–S–H_2O, and Mo–S–H_2O systems (Figure 4) provided strong thermodynamic validation of the experimental pathway. The diagrams confirmed that:

- MoO_4^{2-} is stable over a large pH–Eh region, explaining its rapid extraction from acidic leach solution.
- NiS is stable at moderately reducing potentials and mid-range pH, consistent with its early precipitation.
- CoS stability occurs at slightly more oxidizing conditions, accounting for its later precipitation.

These stability patterns match observations reported across the literature, reinforcing the rationale for the Mo → Ni → Co separation strategy.

3.6 Comparative Performance of the Integrated Flowsheet

Our experimental results match recent high-performance hydrometallurgical data. The integrated flowsheet achieved the following recovery efficiencies:

- Mo: 98–99.5%
- Ni: 90–94%
- Co: 85–90%

These rates align with values reported for catalyst recycling, industrial sulfate processing, and Mo–Ni–Co recovery systems [1,6,8,13]. Furthermore, the proposed process provides a straightforward, highly selective method for treating actual industrial streams, such as wash solutions from sulfuric-acid plants.

3.7 Industrial and Environmental Implications

This integrated process provides direct practical benefits for industrial facilities:

- Facilities can regenerate and reuse ammoniacal solutions and sulfide reagents, lowering operational costs.
- Sulfide precipitation produces stable, environmentally safe materials.
- Using IX or SX for Mo extraction minimizes organic reagent consumption and secondary waste.
- The flowsheet directly accommodates the actual chemical compositions of non-ferrous metallurgical wash streams.

These outcomes confirm that the multi-stage system effectively recovers critical metals from complex technogenic sources under real industrial conditions.

4 Conclusion

Our integrated hydrometallurgical approach efficiently and sequentially recovers Mo, Ni, and Co from complex technogenic sulfate solutions and spent catalyst residues. Experimental data and thermodynamic analyses from thirteen peer-reviewed sources validate this separation strategy, which leverages the inherent chemical differences of these metals.

In the first stage, we selectively extracted molybdenum (predominantly present as soluble molybdate) using anion-exchange resins or tertiary amine extractants, achieving >98% extraction efficiency. Removing Mo before processing Ni and Co minimizes downstream interference and enhances the flowsheet's overall selectivity.

Subsequent ammoniacal leaching dissolved nickel effectively by forming stable ammine complexes, whereas cobalt remained largely insoluble. This step yielded a Ni-rich solution with minimal Co, Fe, Al, and Mn contamination. Our calculated selectivity coefficients (β = 3.4–4.6) match literature values, validating ammoniacal leaching as a critical separation stage.

We utilized distinct stability windows during sulfide precipitation to recover NiS and CoS step-by-step. NiS precipitated under moderately reducing conditions (pH 3.5–4.2), while CoS required slightly higher pH and Eh levels. This precipitation behavior aligns seamlessly with thermodynamic Eh–pH stability fields, confirming the sequential Ni → Co separation.

Our final metal recoveries (98–99.5% for Mo, 90–94% for Ni, and 85–90% for Co) meet or exceed standard industry values for catalyst recycling and sulfate treatment. This streamlined flowsheet cuts reagent consumption, limits impurity co-precipitation, and generates stable sulfide products ready for metallurgical upgrading.

Ultimately, this multi-stage process provides a practical, environmentally safe method for recovering critical metals from industrial technogenic solutions. Because the outcomes closely track both experimental and thermodynamic predictions, the flowsheet is highly scalable for industrial hydrometallurgical operations, specifically in non-ferrous smelting and sulfuric-acid production facilities.

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