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Supporting Information

Optimized two-step sulfuric acid leaching for sustainable recovery of valuable metals from hazardous sodium carbonate roasting-leaching residues of spent hydrodesulfurization catalysts

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1. Materials and methods

1.1. Materials

Sodium carbonate (Na₂CO₃) roasting-leaching residues from spent petroleum catalysts (CoMo/ Al₂O₃) were collected from a facility in Zhejiang Province, China, following primary extraction of molybdenum (Mo). The residues were dried at 105 °C, ground to a particle size finer than 200 mesh, and stored in a desiccator before use. All chemicals employed—including sulfuric acid (H₂SO₄), hydrogen peroxide (H₂O₂), nitric acid (HNO₃), potassium sulfate (K₂SO₄), and ethylene glycol (EG)—were of analytical grade. Deionized water was used for all dilutions and washing steps.

1.2. Leaching procedures

Leaching tests were performed in a four-neck round-bottom flask equipped with a heating mantle, temperature probe, condenser, constant-pressure funnel, and mechanical stirrer. Samples of various weights were leached, followed by vacuum filtration. Residues from leaching were rinsed, dried, and preserved for subsequent characterization. The elemental composition of the filtrates was quantified by inductively coupled plasma optical emission spectrometry (ICP-OES). Residual EG and nitrate ions (NO₃⁻) were measured using a total organic carbon analyzer (TOC) with an integrated total nitrogen (TN) module.

1.3. Characterization

Comprehensive characterization of the Na₂CO₃ roasting-leaching residues was conducted to identify phase composition, morphology, and elemental distribution. As shown in Fig. S1, X-ray diffraction (XRD) analysis indicated the primary crystalline phases to be aluminum oxide (Al₂O₃) in corundum and alumina forms, molybdenum disulfide (MoS₂), molybdenum oxide (MoO₃), cobalt(II) oxide (CoO), and cobalt(III) oxide (Co₂O₃). Morphological and elemental insights were obtained using scanning electron microscopy (SEM) coupled with energy-dispersive spectroscopy (EDS), confirming the main constituents as cobalt (Co), molybdenum (Mo), and aluminum (Al), along with trace silicon (Si), sodium (Na), and phosphorus (P). Solid samples underwent alkali fusion prior to dissolution; subsequently, metal concentrations in aqueous solutions were precisely determined via ICP-OES after appropriate dilution. Sulfur (S) content was measured using a carbon-sulfur analyzer. The complete elemental composition is summarized in Table S1.

Table S1 Chemical compositions of the Na₂CO₃ roasting-leaching residue from spent

Element	Co	Мо	Р	S	Al	Si	Mg
wt%	2.69	1.28	0.88	0.59	28.61	6.07	0.60

HDS catalysts.



Fig.S1. (a) XRD patterns, (b) real-life photo, (c) SEM images, (d, e) elemental distribution, and (f) EDS analysis of the Na₂CO₃ roasting-leaching residue from spent HDS catalysts.

2. Results and discussion

2.1 Optimal conditions of H₂SO₄ leaching

This optimization explored the leaching yields for Co, Mo, and Al using an OA16 $(4^4 \times 2^3)$ design matrix, as outlined in Table S2. This matrix incorporated four variables—H₂SO₄ concentration (A), temperature (B), solid-to-liquid ratio (C), leaching time (D), each with four levels and the three variables: oxidant (E), particle size (F), stirring speed (G)—each at two levels

	Factors									
Level	А	В	С	D	Е	F	G			
	H_2SO_4 concentration (mol L ⁻¹)	Solid-liquid ratio	Temperature (°C)	Time (h)	oxidant	Particle size	stirring speed (rpm)			
1	3	1:3	50	1	Stoichiometric H ₂ O ₂	>200 mesh	200			
2	6	1:6	70	3	no oxidant	original sample	300			
3	9	1:9	90	6	/	/	/			
4	12	1:12	110	9	/	/	/			

Table S2 Levels and factors affecting the leaching yield.



Fig. S2. (a) Effects of oxidants on Al, Mo, and Co leaching; (b) XRD patterns of residues; SEM images of residues from leaching with (c) H_2SO_4 alone, (d) H_2SO_4 with H_2O_2 , and (e) H_2SO_4 with HNO₃. (Conditions: 6 mol L⁻¹ H_2SO_4 , 110 °C, 1:6 solid-to-liquid ratio (w/v), 6 h, >200 mesh, 300 rpm; oxidants at stoichiometric

values.)



Fig. S3. Impact of ethylene glycol (EG) on the leaching efficiencies of Al, Mo, and Co, as well as total organic carbon (TOC) levels, in an H_2SO_4/H_2O_2 system, comparing results at $3 \times (a, b)$ and $5 \times (c, d)$ stoichiometric levels of H_2O_2 . Experimental conditions: 6 mol L^{-1} H₂SO₄, 1:6 (w/v) solid-to-liquid ratio,

110 °C, >200 mesh, 300 rpm, 6 h.

2.2 Circulating leaching method

Table S3. Chemical compositions of the leach liquor obtained after dilution.

Element	Со	Мо	Al	Р	Si	Mg
g L^{-1}	2.85	1.34	26.51	1.25	0.046	0.61

	Factors						
Level	А	В	С				
	Temperature (°C)	Stoichiometric (times)	Time (h)				
1	0	1.0	1				
2	5	1.3	2				
3	10	1.5	4				
4	20	2.0	6				

Table S4. Levels and factors affecting the removal yield of Al.

(a)

(b)



Fig. S4. Crystallization images of KAl(SO₄)₂ ·12H₂O: (a) before washing and (b) after



Fig. S5. Loss ratio of Al with varying stoichiometric H₂O concentrations.

Element	Со	Мо	Al	Р	Si	Mg
$g L^{-1}$	4.79	2.07	28.15	2.64	0.14	1.43

Table S5. Chemical composition of the neutralizing leaching liquor.

Table S6. Chemical compositions of the neutralizing leaching residue.

Element	Со	Мо	Р	S	Al	Si	Mg
wt%	2.40	1.10	0.14	0.88	26.97	11.40	0.12

Table S7. Chemical compositions of the final circulating leaching residue.

Element	Со	Мо	Р	S	Al	Si	Mg
wt%	0.34	0.12	0.022	0.19	20.33	20.71	0.10

Fig.S6. (a) XRD patterns of circulating leaching residues; (b) SEM image and (c) real-life photo of the neutralized residues; (d) SEM image and (e) real-life photo of the final circulating leaching residues.

2.3 Calculation of Co, Mo, and Al recovery rates

2.3.1 Recovery rates during the H₂SO₄ leaching stage

The recovery rate (%) of each metal (Al, Co, Mo) during H₂SO₄ leaching was calculated using the following formula:

Recovery rate (%) =
$$\left[1 - \frac{m_{\rm r} \times \omega_{\rm r}}{m_{\rm i} \times \omega_{\rm i}}\right] \times 100\%$$

where:

 $m_{\rm r}$ —Mass of residue after H₂SO₄ leaching stage (g);

- ω_r —Mass fraction of the metal (Al, Co, Mo) in residue (%);
- $m_{\rm i}$ —Initial mass of the feedstock before leaching (g);
- ω_i —Mass fraction of the metal (Al, Co, Mo) in initial feedstock (%).

2.3.2 Overall recovery rates after circulating leaching

The overall recovery rate (%) of each metal (Al, Co, Mo) after circulating leaching was calculated by:

Overall recovery rate (%) =
$$\left[1 - \frac{m_{\text{cr}} \times \omega_{\text{cr}}}{(m_{\text{nr}} + m_{\text{pr}}) \times \omega_{\text{i}}}\right] \times 100\%$$

where:

 $m_{\rm cr}$ —Mass of residue after circulating leaching (g);

 ω_{cr} —Mass fraction of the metal (Al, Co, Mo) in the circulating leaching residue (%);

- $m_{\rm nr}$ —Mass of newly added feedstock in the circulating step (g);
- $m_{\rm pr}$ —Mass of feedstock previously added during neutralization leaching step (g);
- ω_i —Mass fraction of the metal (Al, Co, Mo) in initial feedstock (%).

2.3.3 Removal rate of Al and entrainment rates of Mo and Co from acidic leachate during crystallization

The removal rate (%) of Al and the entrainment rates (%) of Mo and Co from the acidic leachate during crystallization were determined as follows:

Removal (Al) or Entrainment (Mo, Co) rate (%) = $\left[1 - \frac{m_{\text{mf}} \times \omega_{\text{mf}}}{m_{\text{of}} \times c_{\text{of}}}\right] \times 100\%$

where:

 $m_{\rm mf}$ —Mass of mother liquor after crystallization (g);

 $c_{\rm mf}$ —Concentration of Al, Co, or Mo in the mother liquor (g L⁻¹ or wt%);

 $m_{\rm of}$ —Mass of original acidic leachate before crystallization (g);

 c_{of} —Concentration of Al, Co, or Mo in original acidic leachate (g L⁻¹ or wt%).

(a) H_2SO_4 (b) H_2O_2 EG 0.7%99.3%

2.4 Economic analysis of oxidant selection

Fig. S7 (a) Proportion of reagent cost for the H_2SO_4 - $H_2O_2(5 \times)$ -EG(1%) leaching system and (b) Proportion of reagent cost for the H_2SO_4 -HNO₃(0.25 \times) leaching

system.

Although the leaching efficiency of the $H_2SO_4-H_2O_2(5\times)-EG(1\%)$ system is similar to that of the H_2SO_4 -HNO₃(0.25×) system, there are some key differences. On

one hand, the H_2SO_4 - H_2O_2 -EG system leaves organic residue (TOC), which could interfere with downstream separation and purification processes. On the other hand, the cost of the oxidant H_2O_2 accounts for 19.8% of the total reagent cost, much higher than the 0.7% cost share for HNO₃. Based on preliminary calculations, the cost of the H_2SO_4 - H_2O_2 -EG system is approximately \$16.22 per kg of residues, whereas the H_2SO_4 -HNO₃ system costs \$12.75 per kg of residues. As a result, the reagent cost for the H_2SO_4 - H_2O_2 -EG leaching system is 27.2% higher than for the H_2SO_4 -HNO₃ system. Therefore, using HNO₃ as the oxidant is considered a more cost-effective experimental option.

When HNO₃ is used, it makes up only 0.24 % (v/v) of the leach solution. While trace NO₂ formation is unavoidable, the amount generated is negligible. In industrial settings—and in our pilot trials—any NO₂ is removed by alkaline scrubbers, and the resulting nitrite/nitrate-laden liquor is recycled, effectively minimizing emissions [1, 2]. The key absorption reactions are:

2NaOH+2NO₂=NaNO₃+NaNO₂+ H₂O

NO+NO2+2NaOH=2NaNO2+H2O

References

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[2] N. J. Suchak, K. Jethani and J. B. Joshi, Ind. Eng. Chem. Res., 1990, 29, 1492–1502.