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Recovery of valuable metals from metal-containing spent hydrodesulfurization catalysts by a hydrometallurgical process

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ABSTRACT

This research scheme relates to a new hybrid treatment method for recovering nickel (Ni) and cobalt (Co) metal value from spent hydrodesulfurization catalyst after the recovery of molybdenum (Mo) and vanadium (V) by the 4Hs and solvent extraction purification processes. The influences of solid/liquid ratio (S/L), spontaneous exothermic reaction temperature, reaction time, and additive agents were investigated. The insoluble matter obtained after treatment of the 4Hs process was characterized and elements were recovered by solvent extraction purification techniques. The blue sludge with H_2O_2-oxidation, hot, H_2SO_4-leaching, and H_2O-exothermic reaction (the 4Hs), and solvent extraction hybrid treatment processes allowed good recovery of valuable metals. The results reveal that not only was the filtrate essential for the recovery, separation, and purification of Ni and Co with a high yield of over 85%, but also the solid product of aluminum sulfate ($Al_2(SO_4)_3$) after filtration was transformed into aluminum oxide (Al_2O_3) by adding ammonium sulfate agent ($NH_4(SO_4)_3$) and drying. The 4Hs process was used following the inverse mixing method.

Keywords: Spent hydrodesulfurization catalyst; Blue sludge; Hydrometallurgy; Solvent extraction; Nickel; Cobalt

1. Introduction

The petroleum refining industry makes extensive use of catalysts for the desulfurization of the various oil fractions. Catalysts used for hydrodesulfurization (HDS) contain critical and toxic metal components, such as Ni, V, Mo, and Co, and are generally supported by alumina (boehmite) [1,2].

The catalysts deactivate with time, and when the activity of the catalyst declines below the acceptable level, it is usually regenerated and reused. The life cycle time of an HDS catalyst, after several intermediate regeneration operations, is from 3 to 24 months. It is estimated that more than 10,000 tons of spent HDS catalysts are generated annually by the China Petroleum Corporation (CPC) and Formosa Petrochemical Corporation (FPCC) in Taiwan [3]. Thus, the quantity of blue sludge produced yearly by roasting with Na_2CO_3 agent from three spent HDS catalysts recycling treatment companies is estimated to be 7,000 tons/year, while the nickel and cobalt content in blue sludge have been found to be 3% and 0.5%, respectively.

Spent HDS catalysts are usually regenerated two or three times before being discarded. Various methods of handling these spent HDS catalysts are available to refiners, and they can be used as a source of secondary raw material [1,4–6]. Nevertheless, spent HDS catalysts contribute a significant amount of the solid wastes generated in the petrochemical industry. These spent catalysts have been discarded for landfill in the past, but environmental pollution of soil contaminated by these has become a serious problem. Increasing

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environmental concerns and legislation regarding the disposal of hazardous residues are forcing companies and countries to process their own waste products and residues. Spent HDS catalysts have been classified as hazardous wastes by the EPA in the USA. In short, the spent HDS catalyst wastes have become an environmental problem, and at the same time they present an opportunity for the development of a new business to rejuvenate, recycle, and convert them into environmentally acceptable safe materials for recycling [1,4,5,7]. Several alternative methods, such as disposal in landfills, reclamation of metals, regeneration/rejuvenation and reuse, and utilization as raw materials to produce other useful products, are available to help refiners to deal with the problem of spent catalysts [5,7,8]. These processes can be broadly classified into the following four groups: (1) minimization of spent HDS catalyst waste generation, (2) utilization to produce new catalysts and other useful materials, (3) recycling through recovery of metals, and (4) treatment of spent catalysts for safe disposal. In previous papers, the main processes used for recovering metals from spent HDS catalysts are roasting and solvent extraction purification, but there is a low yield with these approaches. Moreover, the main part of the catalyst, carrier Al_2O_3, has a low level of recovery, thus still causing pollution.

The proposed hydrometallurgical treatment process has three potential advantages: (1) Recovery of the valuable materials of Ni, Co, and $Al_2(SO_4)_3$ from blue sludge. (2) A high yield of over 80% can be obtained from this process, which is because the spinel structure was destroyed, and this may be attributed to the strong spontaneous exothermic reaction temperature that occurs due to the inverse treatment approach (i.e., adding drops of hot water to concentrated sulfuric acid solution). (3) The hybrid treatment procedure will help reduce the environmental burden and have greater economic benefits. Therefore, the development of this new, feasible, and sustainable process can not only treat spent HDS, but also recover valuable metals, such as Al, Ni, and Co.

The aim of this study is to investigate and discuss the feasibility of recovering of valuable materials from Ni-containing spent HDS catalysts after the recovery of Mo and V by a hydrometallurgical process. The proposed 4Hs process is compared with the conventional mixing of acidic leaching method (adding concentrated sulfuric acid agent to hot water), and the inverse approach (adding drops of hot water to concentrated sulfuric acid solution) seems to better able to dissolve $NiAl_2O_4$ and $CoAl_2O_4$ and effectively destroy the spinel structure.

2. Experimental

2.1. Characterizations

Spent catalyst was obtained from the residue HDS unit of Hong Jing Environment Company (Pingtung County, southern Taiwan) for this research work, and was characterized for its composition and pH value. The determination of the heavy metal concentrations of blue sludge, solution after solvent extraction, and the solid product after filtration from the 4Hs process was carried out using ICP-OES. The solid product after filtration from the 4Hs process was characterized with X-ray diffraction (XRD).

2.2. Analytical methods

An X-ray diffractometer (XRD, Bruker AXS-D8A) was used to examine and scan the crystalline phases of the recovery product after filtration from the 4Hs process from 10° to 80° (2θ) at a scan rate of 4°/min. In the scanning electron microscope (SEM, Hitachi 3000) analysis, a small amount of recovery product was dispersed in ethyl alcohol and shaken in an ultrasonic machine for 10 min.

2.3. Experimental apparatus and treatment procedure

A schematic diagram of the experimental procedure for blue sludge hybrid treatment using the 4Hs and solvent extraction purification processes is shown in Fig. 1, and this can be divided into two stages. The first is the pretreatment and 4Hs processes (including H_2O_2-oxidation, hot, H_2SO_4-leaching, and H_2O-exothermic reaction), and the second is the solvent extraction purification process stage (extraction and stripping).

2.3.1. The pretreatment and 4Hs processes

First of all, each sample of blue sludge was dried, ground, and sieved in the pretreatment process. After milling, the particles had a diameter of less than 210 μm (ASTM No. 70). After the pretreatment process the blue sludge was stirred in 1,000 mL of 31 wt% hydrogen peroxide agent (H_2O_2; a liquid to solid ratio of 2) at 300 rpm for 20 min to form an oxidative and homogeneous suspension. Then, the temperature of the

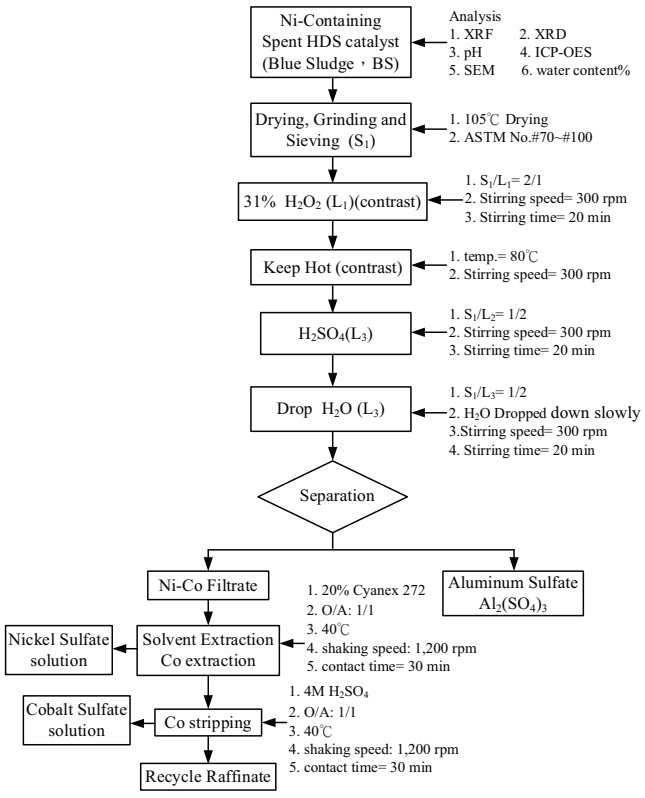

Fig. 1. Flowchart of overall hybrid treatment method including the 4Hs and solvent extraction purification processes.

suspension was continuously increased to 80°C during the 4Hs experimental process.

1,000 mL of 98 wt% sulfuric acid agent was added to the suspension, and the optimized conditions were as follows: a liquid to solid ratio of 2, reaction time of 20 min, and stirring rate of 300 rpm.

The main reason why the spinel structure was destroyed was due to the strong spontaneous exothermic reaction temperature. After completion of the 4Hs process, solid–liquid separation was carried out by filtration, and the residue was transformed into aluminum oxide (Al_2O_3) with the addition of ammonium sulfate agent ($NH_4(SO_4)_3$), and then dried.

2.3.2. Solvent extraction purification process

The commercial extractant, Cyanex 272, with the active component of $C_{16}H_{34}PO_2H$ (bis(2,4,4-trimethylpentyl)phosphinic acid), was used as-received, without further purification. Cyanex 272 has an average molecular weight of 290.43, and density of 0.92 g/cm^3, with 85 wt% active component concentration.

In the following solvent extraction of the leachate, a selective extraction of Co into the organic phases was achieved by using Cyanex 272 as the extractant while Ni remained in the aqueous phase. The following parameters were adopted: the pH of the aqueous phase was adjusted to 6.0, the concentration of Cyanex 272 was 20%, the shaking frequency was 1,200 rpm, the contact time was 30 min, and the O:A phase ratio was 1:1.

3. Results and discussion

3.1. Characterizations of blue sludge

The characterizations of the blue sludge are shown in Table 1. The amount of aluminum in the blue sludge was 25.63%, while the main recyclable metals were 0.33% of Co, 0.78% of V, 1.85% of Ni, and 0.36% of Mo. The other trace elements, such as Fe and Zn, ranged from 0.63% to 0.10%. The water content, ash content, and inflammable content had weight percentages of 29.98%, 68.91%, and 1.11%, respectively. Therefore, the development of a hydrometallurgical process for the recovery of Ni and Co from spent HDS catalyst is important to avoid environmental pollution and promote the circular use of resources.

3.2. Extraction efficiency of Ni and Co and the purification process

The conventional combinations of acidic leaching processes for removing heavy metals from blue sludge are shown in Table 2. For Ni and Co, the order of the extraction efficiency for equal solid to liquid ratios of acid was HNO_3 > H_2SO_4 > HCl. The addition of H_2O_2 as a reducing agent and heating to 80°C also improved the extraction efficiency. However, the extraction efficiency for blue sludge when using the conventional mixing of acidic leaching processes was still less than 60% for Ni and 50% for Co. Therefore, the recovery of the valuable materials (Ni, Co, and $Al_2(SO_4)_3$) using the proposed approach, with a high yield over 80% from spent HDS (Al_2O_3-based) catalysts, is of obvious important for recycling and sustainable development.

The novel 4Hs process presented in this work was compared with the conventional mixing of acidic leaching method (as shown in Table 3). The extraction efficiency of Ni and Co from blue sludge using the 4Hs process was significantly higher than that seen with the conventional mixing of acidic leaching method. The amount of Al extraction varied between 88.5% and 98.7%, Ni between 88.2% and 95.3%, and Co between 78.5% and 85.6%. Extraction with the 4Hs process showed the best compromise among the extraction efficiencies for Al, Ni, and Co from spent HDS catalyst after the recovery of Mo and V. The addition of drops of hot water into the concentrated sulfuric acid solution was able to more effectively destroy the spinel structure. Therefore, the 4Hs process can more effectively recover valuable metals such as Al, Ni, and Co compared with the conventional processes.

Recovery rates of up to 98% for Ni and 85% for Co in separate solutions of the solvent extraction purification process were achieved in this work, using low cost and easily available extraction (Cyanex 272, pH 6.0) and stripping (H_2SO_4, pH 4.1) reagents.

Table 1
Characteristics and composition of blue sludge

Item	Blue sludge
pH	10.37 ± 0.28
Water content (%)	29.98 ± 1.54
Ash content (%)	68.91 ± 2.35
Combustible content (%)	1.11 ± 0.21
Element (mg/kg)	
Al	256,328 ± 3,646
Co	3,306 ± 23
V	7,827±102
Ni	18,453 ± 370
Mo	3,590 ± 68
Fe	6,347 ± 81
Zn	1,025 ± 22

Table 2
Extraction efficiency of Ni and Co from blue sludge after the recovery of Mo and V at different acid extraction conditions

Acid	Extraction conditions	Ni (%)	Co (%)
37% HCl	S/L: 1/2, 300 rpm for 1 h	39.8	34.5
37% HCl	S/L: 1/2, heated at 80°C and 300 rpm for 1 h	48.0	39.0
98% H_2SO_4	S/L: 1/2, 300 rpm for 1 h	45.0	38.3
98% H_2SO_4	S/L: 1/2, heated at 80°C and 300 rpm for 1 h	52.5	42.7
98% H_2SO_4	S/L: 1/2, adding H_2O_2 as reducing agent, heated at 80°C and 300 rpm for 1 h	57.0	48.8
68% HNO_3	S/L: 1/2, heated at 80°C and 300 rpm for 1 h	54.0	44.7

Table 3
Extraction efficiency of Al, Ni, and Co from blue sludge after the recovery of Mo and V at different stages of the 4Hs process

1H H_2O_2	2H Heat (°C)	3H H_2SO_4	4H Hot water	Recovery (%)		
				Al	Ni	Co
–	–	S/L: 1/2	S/L: 1/2	88.5	88.2	78.5
–	80	S/L: 1/2	S/L: 1/2	96.8	94.0	83.5
S/L: 1/1	–	S/L: 1/2	S/L: 1/2	90.0	89.8	80.1
S/L: 1/1	80	S/L: 1/2	S/L: 1/2	94.9	92.5	82.9
S/L: 1/2	–	S/L: 1/2	S/L: 1/2	93.4	87.7	82.5
S/L: 1/2	80	S/L: 1/2	S/L: 1/2	98.7	95.3	85.6

Reaction conditions: 300 rpm, 20 min for 1H, 20 min for 3H, and 20 min for 4H.

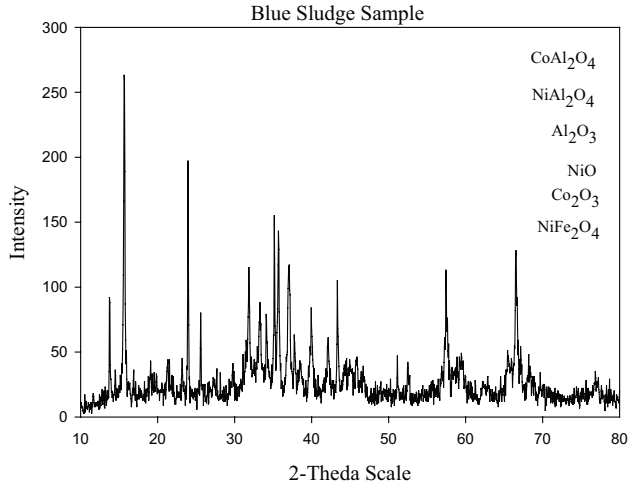

Fig. 2. XRD pattern of the blue sludge sample.

3.3. XRD and SEM analysis of blue sludge

The crystal phase of blue sludge was determined by XRD analysis, and the XRD pattern is shown in Fig. 2, which corresponds to the crystalline structure of spinel oxides, with the oxides being $CoAl_2O_4$, $NiAl_2O_4$, $NiFe_2O_4$, NiO, Co_2O_3, and Al_2O_3. The spinel crystalline structure is the same as the cubic spinel (AB_2O_4), in which A^{2+} and B^{3+} are replaced by the non-ferrous metals M^{2+} and Al^{3+}, respectively. As such, MAl_2O_4 is generally defined as the chemical formula of the spinel's crystalline structure [9]. Due to its high stability, ferrites form easily during the treatment of heavy metal-containing wastewater and sludge by wet oxidation [10].

Fig. 3 shows the SEM image of the blue sludge sample. It can be clearly observed that blue sludge has a spherical, ellipsoid, or granular structure with particles that are an average 20–30 μm in width and 40–60 μm in length. This indicates that the blue sludge was piled together intensely, in many tiny particles. The energy-dispersive spectrum analysis further proves that after roasting the blue sludge sample with Na_2CO_3 agent from a recycling treatment company then the resulting material is composed of O, Al, Ni, Co, V, Mo, Fe, Zn, and Na elements.

The crystal phase of the recovered solid product was determined by XRD analysis, with the results shown in Fig. 4. This pattern corresponds to the crystalline structure of aluminum metal, and the aluminum oxides are Al and Al_2O_3.

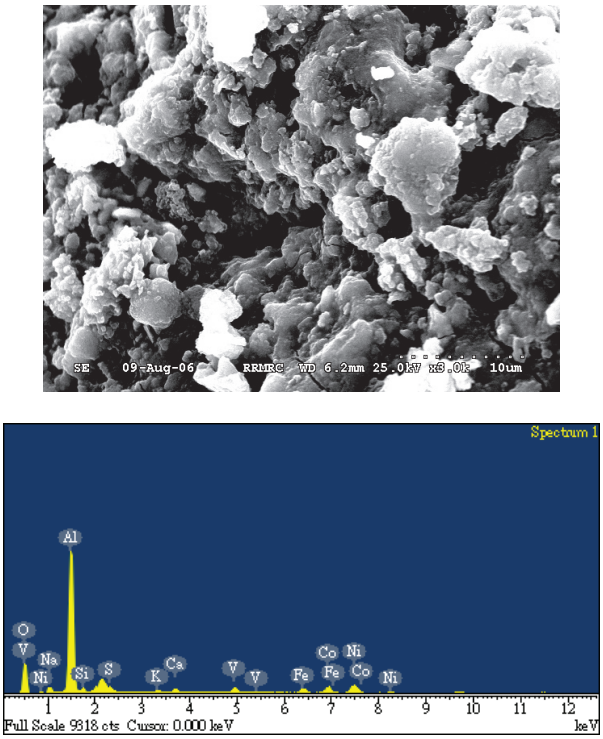

Fig. 3. SEM image of the blue sludge sample.

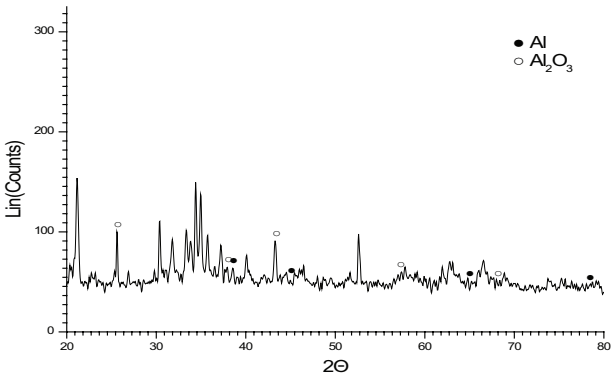

Fig. 4. XRD pattern of the solid product of aluminum (Al) and aluminum oxide (Al_2O_3).

Table 4
Economic estimation for a recovery plant of spent hydrodesulfurization catalyst treatment using the 4Hs process

Item	Million (NTD)	Month
Capital cost	10.0	–
Operating and maintenance cost per month	20.6	–
Revenue from treatment fee and sales of resources per month	21.6	–
Net profit per month	1.0	–
Period of return[a]	–	10

[a]$e = a/(b - c)$.

3.4. Economic estimation

The preliminary economic estimation for a recovery plant for the treatment of spent HDS catalyst using the 4Hs process with a capacity of 7,000 tons/year (about 25 tons/d) is shown in Table 4. The capital cost would be NTD $10 million, the annual operating and maintenance cost NTD $246.9 million (including the consumption cost of H_2SO_4 and H_2O_2), and the annual amortization cost NTD $1.5 million. The landfill fees for spent HDS would be NTD $28 million/year. Annual profits from treatment fees and sales of Ni and Co metals would be NTD $259.5 million (75% of Ni or Co recovery). The total investment could thus be reimbursed within 1 year. Consequently, the 4Hs process is economically feasible for the recovery of spent HDS.

4. Conclusion

It is estimated that more than 10,000 tons of spent HDS catalysts are generated annually by the CPC and FPCC in Taiwan. The quantity of blue sludge produced yearly by three spent HDS catalyst recycling treatment companies is thus estimated to be 700 tons/year, while the nickel and cobalt content of blue sludge have been found to be 3% and 0.5%, respectively. The novel 4Hs process is compared with the conventional acidic leaching method, and the inverse approach (adding drops of hot water to concentrated sulfuric acid solution) seems to better dissolve $NiAl_2O_4$ and $CoAl_2O_4$ by more effectively destroying the spinel structure. The main advantage of this approach is that it can be used to recover the valuable materials of Ni, Co, and $Al_2(SO_4)_3$ from blue sludge, with a high yield of over 80% due to the destruction of the spinel structure, which is attributed to the strong spontaneous exothermic reaction temperature. The proposed hybrid treatment procedure can thus help reduce the environmental burden and have economic benefits.

References

[1] A. Akcil, F. Vegliò, F. Ferella, M.D. Okudan, A. Tuncuk, A review of metal recovery from spent petroleum catalysts and ash, Waste Manage., 45 (2015) 420–433.
[2] S.P. Barik, K.H. Park, P.K. Parhi, J.T. Park, C.W. Nam, Extraction of metal values from waste spent petroleum catalyst using acidic solutions, Sep. Purif. Technol., 101 (2012) 85–90.
[3] K. Lan, Catalyst Recycling: Green Competitiveness for the Petrochemical and Automobile Industries, CTIMES, 2015. Available at: https://en.ctimes.com.tw/DispArt.asp?k=green-technology/UWin-Nanotech&o=1510071126U1
[4] Z. Li, M. Chen, Q. Zhang, X. Liu, F. Saito, Mechanochemical processing of molybdenum and vanadium sulfides for metal recovery from spent catalysts wastes, Waste Manage., 70 (2017) 734–738. Available at: http://dx.doi.org/10.1016/j.wasman.2016.06.035
[5] T.H. Nguyen, M.S. Lee, Development of a hydrometallurgical process for the recovery of calcium molybdate and cobalt oxalate powders from spent hydrodesulphurization (HDS) catalyst, J. Cleaner Prod., 90 (2015) 388–396.
[6] B. Singh, Treatment of spent catalyst from the nitrogenous fertilizer industry—a review of the available methods of regeneration, recovery and disposal, J. Hazard. Mater., 167 (2009) 24–37.
[7] V. Ruiz, E. Meux, S. Diliberto, M. Schneider, Hydrometallurgical treatment for valuable metals recovery from spent $CoMo/Al_2O_3$ catalyst. 1. Improvement of soda leaching of an industrially roasted catalyst, Ind. Eng. Chem. Res., 50 (2011) 5295–5306.
[8] V. Ruiz, E. Meux, M. Schneider, V. Georgeaud, Hydrometallurgical treatment for valuable metals recovery from spent $CoMo/Al_2O_3$ catalyst. 2. Oxidative leaching of an unroasted catalyst using H_2O_2, Ind. Eng. Chem. Res., 50 (2011) 5307–5315.
[9] M.N. Barroso, M.F. Gomez, L.A. Arrúa, M.C. Abello, Reactivity of aluminum spinels in the ethanol steam reforming reaction, Catal. Lett., 109 (2006) 13–19.
[10] D.H.K. Reddy, Y.S. Yun, Spinel ferrite magnetic adsorbents: alternative future materials for water purification? Coord. Chem. Rev., 315 (2016) 90–111.