J. of Korean Inst. of Resources Recycling
Vol. 22, No. 4, 2013, 3-11
http://dx.doi.org/10.7844/kirr.2013.22.4.3
pISSN : 1225-8326 eISSN : 2287-4380

≫ 總　　說 ≪

廢觸媒 酸性浸出液으로부터 溶媒抽出에 의한 몰리브덴과 바나듐의 回收

응우엔 티홍 · †李晩承

木浦大學校 工科大學 新素材工學科 稀有金屬硏究所

Recovery of Molybdenum and Vanadium from Acidic Leaching Solution of Spent Catalysts by Solvent Extraction

Hong Thi Nguyen and †Man Seung Lee

Department of Advanced Material Science & Engineering, Institute of Rare Metal, Mokpo National University, Chonnam 534-729, Republic of Korea

요　　약

폐촉매를 침출한 산성용액으로부터 용매추출에 의해 몰리브덴과 바나듐을 회수하는 공정을 조사하였다. 여러 침출액중 황산용액이 두 금속의 회수측면에서 가장 적합하다. 다른 불순물이 혼합된 용액과 순수한 몰리브덴과 바나듐용액에서 여러 추출제(양이온, 중성, 아민, 양이온과 중성 혼합추출제)에 의한 두 금속의 추출 및 탈거 거동을 검토하였다. 각 추출제는 금속 분리와 제 3상의 형성측면에서 장단점을 지니고 있다. 폐촉매의 산성 침출액으로부터 몰리브덴과 바나듐을 분리회수하는데 있어서 양이온과 중성의 혼합추출제가 가장 적합하다.

주제어 : 폐촉매, 침출, 용매추출, 몰리브덴, 바나듐

Abstract

The recovery of molybdenum and vanadium from acid leaching solutions of spent catalysts using solvent extraction has been investigated. Among various acid leaching solutions, sulfuric acid solution is found to be adequate for the recovery of these two metals. The extraction and stripping behavior of the two metals in the absence and presence of other impurity metals by various types of extractants such as cationic, solvating, amine and a mixture of cationic and solvating extractants was discussed. Each type of extractants has advantage and disadvantage in terms of the possibility of separation and of forming a third phase. Among the various types of extractants, a mixture of cationic and solvating extractants seems to be the most promising extractant system for the separation of Mo and V from the acid leaching solutions of spent catalysts.

Key words : spent catalysts, leaching, solvent extraction, molybdenum, vanadium

* Received : February 15, 2013 · Revised : April 1, 2013 · Accepted : April 16, 2013
†Corresponding Author : Man-Seung Lee (E-mail : mslee@mokpo.ac.kr)
Department of Advanced Materials Science & Engineering, Mokpo National University, 61 Dorim-ri, Chungkye-myun, Muan-gun, Chonnam, 534-729, Korea
Tel : +82-62-450-2492 / Fax : +82-62-450-2498

1. Introduction

Molybdenum and vanadium are important metals used in many technological fields. Molybdenum is a strategic metal which is used in radios, thermocouples, anticathode of X-ray tubes and in the production of special steels.[1] The most important use of vanadium is as an additive for steel. Vanadium compounds are also used in the ceramics industry, in the printing and dyeing of fabrics and in the manufacture of aniline black. In recent decades, the recovery of molybdenum and vanadium from spent catalysts has attracted much attention because large amount of rare metals such as Mo, V, Co, and Ni are contained in the spent catalysts.[2] The spent catalysts mostly consist of molybdenum oxide mixed mainly with vanadium oxides, cobalt or nickel on an alumina carrier. Spent catalysts can be classified into four types like Mo-Fe, Mo-Ni, Mo-Co and Mo-V according to the composition of catalysts.

Reviews on the recovery of Mo and V from spent catalysts have been reported by Zeng and Cheng.[3,4] Molybdenum, vanadium and other metals from spent catalysts were dissolved by leaching and then were recovered from the leaching solutions using conventional separation techniques such as precipitation, adsorption, ion exchange and solvent extraction. It was indicated that acid leaching was used commonly in industry because all of the valuable metals can be dissolved in acid medium. In the separation step, solvent extraction has been found to be the most promising method for the commercial production of the above metals with high purity. Lots of work on the recovery of Mo and V from acid media containing impurities has been conducted using solvent extraction. However, few reviews have been reported to summarize the results. Hence in present review, the results for the extraction and recovery of Mo and V from acid media containing impurities using solvent extraction were summarized in detail.

2. Acid leaching of spent catalysts

In the recovery of metals, several dissolution processes such as acid leaching, caustic leaching, and bioleaching are employed. Each process has suffered several drawbacks but in general acid leaching seems to be more suitable for dissolving all of the valuable metals in the spent catalyst.[3] Among acid leaching process, sulfuric and hydrochloric acid were used commonly.

The leaching of spent catalyst was carried out by varying the concentrations of sulfuric acid from 30 to 70% (v/v) in the temperature range of 100-200ºC and more than 90% of metals was dissolved.[5] Mihashi[6] reported that most nickel and cobalt could be leached using the mixture of 5 g/L H_2SO_4 and 20 g/L H_2O_2. Siemens[7] has used 10% w/w sulfuric acid leaching for the recovery of molybdenum and nickel from a molybdenum-nickel catalyst. Most of Mo, Ni, and V were dissolved from spent petroleum catalyst using 1 M H_2SO_4 in a single stage within 1h of reaction time[8]. Leaching of Mo and Co from spent catalyst with sulfuric acid alone was not so efficient as with the mixture of sulfuric acid and hydrogen peroxide and with the mixture of nitric acid.[9,10] The leaching percentage of Mo with these two cases was the same while that of cobalt with H_2SO_4-HNO_3 was little higher than in the case of H_2SO_4-H_2O_2. Ognyanova[11] concluded that the acidic leaching had an advantage over alkaline leaching because of cheaper price. The author used sulfuric acid as a leaching reagent for the dissolution of Ni, V and Fe from spent catalysts. Using 6 M H_2SO_4 at 90ºC, most vanadium from vanadium ore was dissolved into the solution.[12]

Hydrochloric acid leaching has been found to have some advantage over other acids in that separation of metals from acidic chloride solution is possible.[3] Ward[13] has used hot concentrated hydrochloric acid to recover metals from spent catalysts. Most metals from spent catalyst was dissolved using hot hydrochloric acid when the temperature was higher than 90ºC. Sefton[14] also used hydrochloric acid for leaching of Mo, V, Co, Ni and Al from spent catalyst. 3M HCl was optimum condition for the leaching of metals from spent catalyst containing these metals.[15,16]

By comparing the leaching efficiency of HCl and H_2SO_4, Zeng and Cheng[3] concluded that although hydrochloric acid leaching was more efficient than sulfuric acid leaching, sulfuric acid leaching was more useful because of more flexible material allowance for the construction of reactors, lower cost and better recirculation possibilities.

3. Molybdenum and vanadium speciation in aqueous solution

The species of molybdenum and vanadium in aqueous solution can be categorized as cationic species, neutral species

and anion species. Zheng and Cheng[4] reported that the anionic species of molybdenum including $Mo_7O_{21}(OH)_3^{3-}$, $Mo_7O_{23}(OH)^{5-}$, $Mo_7O_{22}(OH)_{12}^{4-}$ and MoO_4^{2-} are stable in the pH range from 1 to 6. Vanadium is mostly in the form of anionic species such as $V_{10}O_{27}(OH)^-$, $V_{10}O_{26}(OH)^{2-}$, $V_{10}O_{28}^{6-}$, $V_3O_9^{3-}$, $V_4O_{12}^{4-}$ and $VO_3(OH)^{2-}$ in the pH range from 2 to 9. The cationic species of molybdenum and vanadium is stable in the pH range $0 < pH < 2$ while a small fraction of neutral specie like H_2MoO_4 and $VO(OH_3)$ exist at $pH < 3$. In a solution with 2 to 3 M acid concentration, $VOCl_3^-$, $MoO_2Cl_3^-$ and $MoO_2(SO_4)_2^{2-}$ are formed while neutral species of MoO_2Cl_2, $VOCl_2$ and VO_2Cl are predominant in high acid concentration.[4,17]

Molybdenum and vanadium species in aqueous phase has been studied by Nekovář and Schrötterová.[18] Equilibria involing MoO_4^{2-} protonation are described as follows:

$$7MoO_4^{2-} + (8 + n)H^+ = Mo_7O_{24-n}(OH)_n^{(n-6)-} + 4H_2O,\ (n = 0,\ 1,\ 2,\ 3) \quad (1)$$

Under low concentration of molybdenum, monomeric forms are formed

$$MoO_4^{2-} + kH^+ = H_kMoO_4^{(2-k)-},\ (k = 1,\ 2) \quad (2)$$

With a minimum solubility occurring at about pH 1.5, crystalline MoO_3 is in the equilibrium with MoO_4^{2-}

$$MoO_4^{2-} + 2H^+ = MoO_3(s) + H_2O \quad (3)$$

Polymeric and monomeric species of V are formed by the following Eqs. 4-5

$$10\ VO_2^+ + 8H_2O = V_{10}O_{28-n}(OH)_n^{(6-n)-} + (16-n)H^+,\ (n = 0,\ 1,\ 2) \quad (4)$$

$$VO_2^+ + 2H_2O = VO_{4-m}(OH)_m^{(3-m)-} + (4-m)H^+,\ (m = 0,\ 1,\ 2,\ 3) \quad (5)$$

In the region between decanadates and monomeric species, the formation of $V_kO_{3k}^{k-}$ occurs (Eq. 6)

$$kVO_2^+ + kH_2O = V_kO_{3k}^{k-} + 2kH^+,\ (k = 3,\ 4) \quad (6)$$

When solution pH is low, V_2O_5 precipitates according to the following Eq. 7.

$$2V_kO_{3k}^{k-} + H_2O = V_2O_5 + 2H^+ \quad (7)$$

In sulfuric acid leaching solution, VO_2^+ is acting as an oxidant and hydrolyzes easily to form oxy-anion, releasing protons to make up a series of partially protonated poly-anions.[19] Li[20] reported that vanadium species in aqueous solution depends on several factors, such as solution pH value, vanadium concentration, and its valence. Vanadium is mostly in the form of cationic species VO_2^+ and $H_2V_{10}O_{28}^{4-}$ at $pH < 2.0$ containing 2-3 g/L while VO^{2+} are formed in the same pH range. According to Chagnes[21], in non-complexing aqueous acidic media ($pH < 1$), VO_2^+ is predominant and for $pH > 0.6$, vanadium precipitate as V_2O_5. However in the presence of sulfate/hydrogenosulfate anions, both VO_2^+ and $VO_2SO_4^-$ are formed at $pH < 2$. When solution pH is higher than 2.0, vanadium precipitate as V_2O_5.

4. Solvent extraction

4.1. Molybdenum extraction from acidic media containing single metal

Saberyan[22] reported that the extraction efficiency of molybdenum with Cyanex 301 was dependent upon the type and concentration of the aqueous phase acid, extractant concentration, and metal ion concentration. Molybdenum extraction from hydrochloric and nitric acid solutions at $pH > 1.0$ was quantitative irrespective of the concentration of Cyanex 301 while in the case of sulfuric acid system, the extraction behavior of Mo depends strongly on the concentration of Cyanex 301.

Sato[23] also studied the extraction of molybdenum from 0.1 M to 10 M sulfuric, nitric and hydrochloric acids by TOA and TCMAC. The molybdenum extraction with TOA and TCMC at low aqueous acidity was more quantitative than at high aqueous acidity. Especially, TCMC is more efficient than TOA for the molybdenum extraction when the HCl and HNO_3 concentration was lower than 4M and 0.55M, respectively. Whilst TOA offered higher extraction efficiency than TCMC when the sulfuric acid concentration was lower than 4M. At high acid concentration (2-10M), there was little difference in the distribution coefficient of Mo from HCl solution by these extractants. However, TCMAC and TOA could not extract Mo from HNO_3 (1-5 M) and H_2SO_4 (5-10 M) solution, respectively. Moreover, the total chloride and

nitrate concentration had not much effect on the extraction at low aqueous acidity but they were the controlling factor at higher acidity. The extractability was little influenced when the total sulphate concentration was below 1 M.

The polymeric anionic complexes of molybdenum exist in the pH range from 2.0 to 6.5 and it was possible to extract molybdenum from sulfuric acid by primary amine primene JMT.[18] Various heptamolybdadte and octamolybdate anions were rapidly extracted from acidic media (i.e., pH 1 - 4) by Aliquat 336.[24]

4.2. Vanadium extraction from acidic media containing single metal

Sato[25-27] has studied the extraction of vanadium from hydrochloric acid solutions or mixed solutions of hydrochloric acid and lithium by DEHPA, TOA, Aliquat 336, TBP and TOPO. The obtained results indicated that the controlling factor for the vanadium extraction with TOA, Aliquat 336, TOPO and TBP was total chloride ion concentration. The vanadium extraction from single HCl solution reached a peak in the HCl range 5-7 M, but in the mixture of hydrochloric acid and lithium chloride, it increased continuously with the total chloride concentration. By contrast, the total chloride ion concentration had not great effect on the loading behavior of vanadium using DEHPA

The extraction of vanadium from HCl, H_2SO_4 and HNO_3 acid solutions using Aliquat 336 was studied by El-Nadi.[16] The authors indicated that 3M HCl acid solution was the best solution for the extraction of vanadium. Furthermore, the hydrogen ion concentration at 3M chloride ion concentration had no influence on the extraction while the extraction percentage of vanadium decreased with increasing chloride ion concentration from 3 to 5 M at this acidity (3 M). At pH 1.5-2.0, acidic decavanadate species from sulfuric acid media were rapidly extracted by Aliquat 336, but reddish extracted species turned to olive green within a few days while a black-greenish solid precipitated.[24]

Li[28] reported that the predominant existence of vanadium species in sulfuric acid medium is VO^{2+} when pH is lower than 3.0. Therefore, this species was extracted easily by D2EHPA, EHEHPA and Cyanex 272. The extraction ability of extractants decreased in the following order: D2EHPA > EHEHPA > Cyanex 272. Moreover, total sulphate ion concentration had little effect on the vanadium extraction.

Lozono and Juan [19] indicated that the primary amine Primene 81R can extract vanadium from sulphate media in the range pH of 2-2.5 where $HV_{10}O_{28}^{5-}$ is predominant. The overall extraction mechanism is represented as Eq.8. In this process, 5% isodecanol was used as a modifier to avoid the formation of a third phase. The loaded vanadium was stripped with ammonia solution.

$$5[RNH_2]_{org} + 5H^+]_{aq} + [(HV_{10}O_{28})^{5-}]_{aq} \Leftrightarrow [(RNH_3) + 5(HV_{10}O_{28})^{5-}]_{org} \quad (8)$$

Nekovář and Schrötterová[18] studied the extraction of vanadium from sulfuric acid solution by primary amine primene JMT. The extraction behavior of vanadium was similar to that of molybdenum.

4.3. Molybdenum and vanadium extraction from acidic media in the presence of other metals.

4.3.1. Extraction by cationic extractants

Zhang[29] and Zeng and Cheng[30] have used LIX 63 to extract Mo and V from sulfuric acid solution containing Al, Co, Ni and Fe. It was indicated that both Mo and V can be extracted over other metals in the pH range of 1.0-2.0. A pure V(IV) and Mo(VI) solution can be obtained by selectively stripping V and Mo from the loaded LIX 63 using H_2SO_4 and NH_4OH, respectively.[29] By contrast, Zeng and Cheng[30] indicated that Mo(VI) and V(V) from loaded LIX 63 cannot be stripped with strong sulphuric acid solution. Mo(VI) was still not completely stripped although the stripping of V (V) was complete using 10% ammonia solution. Moreover, the authors showed that 1M NaOH solution could strip most of Mo and V from the loaded organic. Both pure molybdenum and vanadium products were obtained by two separation processes. First, vanadium was recovered as ammonium vanadate after the precipitation of vanadium from the strip liquor. Secondly, a pure molybdenum solution was obtained by further removing small amount of vanadium using Aliquat 336 at pH 8.5.

Zhang[31] have studied selective extraction of molybdenum and vanadium from sulfuric acid solution containing Ni, Co and Al using PC88A. The co-extraction of molybdenum and vanadium was obtained at a low pH based on the differences in equilibria and kinetics of

Table 1 Effect of synergistic extraction (Wu[33])

Organic phase composition	Synergistic coefficient (R)			
	Mo	Fe	As	V
10%(v/v) Cyanex-272 + 20%(v/v) secondary caprylic alcohol	0.82	0.83	0.64	0.36
10%(v/v) Cyanex-272 + 10%(v/v) TBP	4.4	0.55	0.56	0.41

extraction between these metals. Li[32] reported that molybdenum and vanadium were quantitatively co-extracted at pH 2.0 using EHEHPA, where molybdenum and vanadium species like MoO_2^{2+} and VO^{2+} is predominant. The extraction reaction of molybdenum and vanadium by EHEHPA at pH 2.0 is represented in Eqs. 9-10. Most of V from the loaded organic was first stripped with 1M H_2SO_4 and then molybdenum stripping was completed by 10 wt% NH_4OH and 15 wt% NH_4Cl.

$$VO^{2+}_{(aq)} + 2(HA)_{2(org)} = VOA_2{\cdot}2HA_{(org)} + 2H^+_{(aq)} \quad (9)$$

$$MoO_2{}^{2+}_{(aq)} + 2(HA)_{2(org)} = MoO_2A_2{\cdot}2HA_{(org)} + 2H^+_{(aq)} \quad (10)$$

Mishra[8] reported that molybdenum and vanadium can be co-extracted over other metals like Ni, Fe and Al from leach liquor at higher pH or individually extracted at low pH ($pH < 0.5$) and high pH ($pH > 2.0$), respectively by LIX 84-I. The molybdenum and vanadium stripping were carried out by using 20% NH_4OH and the mixture of 20% NH_4OH - 2 M $(NH_4)_2CO_3$, respectively. Park[1] also indicated that pH 0.5 was the best condition to extract molybdenum from Ni and Al by LIX-84I. The extraction reaction of molybdenum is represented in Eq. 11.

$$MoO_{2\ aq}{}^{2+} + 2HR_{org} = (MoO_2{\cdot}R_2)_{\ org} + 2H^+_{aq} \quad (11)$$

Wu[33] studied the extraction of molybdenum from leach liquor containing V, As, Fe using cationic extractants. Molybdenum can be extracted over impurities when the initial leach liquor pH was lower than zero using D2EHPA, EHEHPA and Cyanex 272. Moreover, the optimum extractant was found to be Cyanex 272 for Mo and D2EHPA for Fe and V, respectively.

4.3.2. Extraction by neutral extractants

Most molybdenum from 3M HCl leaching solution of spent catalyst was quantitatively extracted while the co-extraction of vanadium did not exceed 3.6% by the use of TOPO.[16] Banda[15,17] reported that TOPO and TBP can extract molybdenum over cobalt and aluminum from 3M HCl leaching solution. The extraction efficiency of molybdenum with TOPO was higher than with TBP but the stripping of molybdenum from loaded TBP is easier than that from the loaded TOPO. Hence, TBP was recommended as an extractant for the separation of molybdenum from Co and Al.

The solvent extraction reaction of molybdenum in hydrochloric acid solution with TOPO extractant can be represented as follows[17].

At lower concentration of HCl

$$H_2MoO_{4\ aq} + TOPO_{org} = H_2MoO_4.TOPOorg \quad (12)$$

At higher concentration of HCl

$$MoO_2Cl_{2\ aq} + 2TOPO_{org} = MoO_2Cl_2.2TOPO_{org} \quad (13)$$

4.3.3. Extraction by anionic extractants

Olazabal[34] reported that Alamine 336 and Aliquat 336 could be used in separating vanadium and moly- bdenum. Molybdenum can be separated completely from vanadium at $pH < 1$ with Alamine 336. Aliquat 336 can be used to extract vanadium in the presence of molybdenum in the pH range from 8 to 9. The authors also showed that stripping efficiency of Alamine 336 was higher than that of Aliquat 336. The simultaneous extraction of Mo(VI) and V(V) by Aliquat 336 has been investigated in the absence and in the presence of phosphate and it has been observed that solid compounds also was slowly precipitated from the loaded organics[24].

A process for the extraction of molybdenum in the presence of other metals from sulfuric acid medium was studied by Valverde Jr [35]. Two extractants were tested: Alamine 304 and Alamine 336. Although both extractants can extract molybdenum when the pH value of acid leaching solution was about 1.8, the best performance was found for Alamine 304. Parhi[36] also has used Alamine

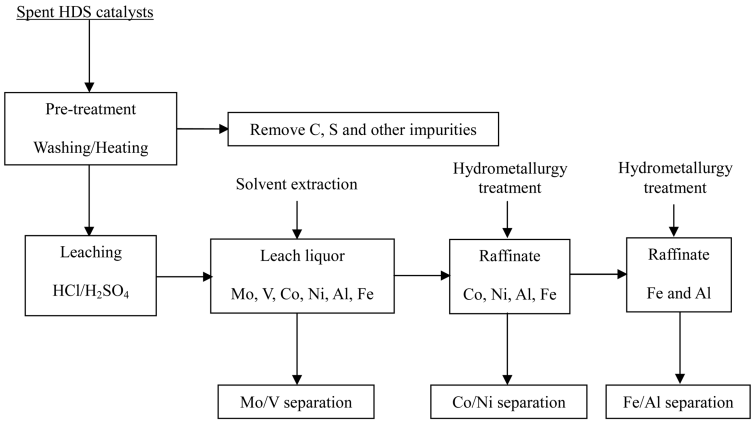

Fig. 1. A general schematic process flow sheet for the recovery of valuable metals from spent catalyst.

304 for recovery of molybdenum in the presence of Co, Ni, Cu and Fe. Most molybdenum was extracted over other metals at pH 1.6. It should be noted that in order to prevent third phase formation or emulsification in the organic medium, the concentration of Alamine 304-I should be below 10% (v/v). Molybdenum from the loaded Alamine 304-I was stripped easily by using 5M NH_4OH-2.5M $(NH_4)_2CO_3$. The extraction reaction of molybdenum in sulfuric acid solution with Alamine 304-I was presented in Eqs.(14) - (16).

$$R_3N_{(org)} + H^+_{(aq)} + HSO^-_{4\,(aq)} \Leftrightarrow R_3NH^+ \text{ --- } [HSO^-_4]_{(org)} \quad (14)$$

$$2\ R_3NH^+ \text{--- } [HSO^-_4]_{(org)} + MoO^{2-}_{4\,(aq)} \Leftrightarrow 2\ [R_3NH^+] \text{ --- } [MoO^{2-}_4]_{(org)} + [HSO^-_4]_{(aq)} \quad (15)$$

$$2R_3N_{(org)} + 2H^+_{(aq)} + MoO^{2-}_{4\,(aq)} \Leftrightarrow 2\ [R_3NH^+] \text{ --- } [MoO^{2-}_4]_{(org)} \quad (16)$$

The selectivity for molybdenum extraction from solution (pH = 2.0) containing copper, magnesium, manganese, iron, cobalt and aluminum with DIDA was carried out by Gerhardt[37]. The co-extraction of iron, cobalt and impurities did not exceed 1-2% while the extraction percentage of copper, manganese and aluminum was negligible.

4.3.4. Extraction by the mixture of cationic and neutral extractant

The main problem encountered during the use of Cyanex 272 is that the extracted Mo-Cyanex 272 forms an insoluble small colloidal particle in the organic phase and secondary caprylic alcohol and TBP were used as a modifiert.[33] Besides preventing the formation of colloidal particle, TBP had a synergistic effect for Mo extraction while there was no effect on the extraction of Mo using secondary caprylic alcohol (Table 1). The authors showed that a mixture of 15% Cyanex 272 and 15% TBP at an equilibrium pH of − 0.05 was adequate for the selective extraction of Mo from leach liquor containing V, Fe and As and the molybdenum from loaded organic was stripped by the use of ammonia solution.

Li[38] reported that D2EHPA could extract vanadium from solution containing Al, Fe and Si when pH value of solution was higher than 1.0. However, the problem for D2EHPA is the formation of third phase due to the hydrolysis of Al(III) and Fe(III) and to the presence of SiO_2 when the initial pH was higher than 2.5. Therefore, TBP was added as an effective phase modifier. The mixture of D2EHPA and TBP was also used to extract vanadium from leach liquor in the presence of iron (II) and other metals.[39,40] Stripping with 15% H_2SO_4 gave high efficiency and the concentration of vanadium in stripping solution can be enriched while the iron concentration can be reduced to 0.6 g/L. Li[20] reported that TBP can be added not only as a phase modifier to inhibit the emulsification of organic phase and the formation of third phase, but also as a synergistic extraction reagent to improve metal extraction compared to single extractant. In vanadium extraction process from sulfuric acid solution containing Fe(III), Fe(II), Mg(II), Al(III) and K(I) by a mixture D2EHPA and TBP, it was suggested

Table 2. A summary of the extraction and stripping of molybdenum and vanadium from acid leaching solution of spent catalyst by some extractants.

Extractant	Extraction		Stripping	
Cationic extractant	40% LIX 63 pH = 1.2 (Mo, V, Al, Co, Ni, Fe)	V 92.09 %; Mo 97.74%	2M H_2SO_4 10% NH_4OH	V 90.51% Mo 97.87 %
	1M LIX 63 pH = 1.4 (Mo, V, Al, Co, Ni, Fe)	> 99 Mo and V	2M NaOH Precipitation V	> 95% Mo and V V 98% ; Mo 96.6%
	15% EHEHPA pH = 2.0 (Mo, V)	V 97.3%; Mo 97.2%	1M H_2SO_4 10wt%NH_4OH+ 15wt%NH_4Cl	V 99% >Mo 99%
	10% LIX 84I; pH =0.5(Mo, Ni, V) 40% LIX 84I; pH =2.6 (Ni, V)	Mo 98% >V 80%	20% NH_4OH NH_4OH-$(NH_4)_2CO_3$	Mo quantitatively > V 99%
	40% LIX 84I pH= 0.5 (Mo, Ni, Al)	Mo 99.9%	1MNH_4OH-1M $(NH_4)_2CO_3$	Mo 98.3%
Neutral extractant	0.05M TOPO 3M HCl solution (Mo, Co, Al)	Mo 99.7%	0.1 M NH_4OH-0.05M $(NH_4)_2CO_3$	Mo 99.7%
	0.5M TBP 3M HCl solution (Mo, Co, Al)	Mo 99.8%	0.1M HCl	Mo 99.3%
Anionic extractant	5 vol.% Alamine 304 pH 1.8 (Mo, Co, Ni, Al, P)	>Mo 99.5%	2M NH_4OH	> Mo 99.95%
	10%(v/v) Alamine304-1 pH 1.62 (Mo, Fe, Cu, Co, Ni)	Mo 99.9%	5M NH_4OH-2.5M $(NH_4)_2CO_3$	Mo 99.97%
	7%(v/v)DIDA pH 2 (Mo, Co, Mg, Mn, Fe, Al)	Mo 95.2%	NH_4OH	
The mixture of cationic and neutral extractant	15% (v/v) Cyanex 272 and TBP pH -0.05 (Mo, Fe, As, V)	Mo 97.4 %	20 wt.% NH_4OH	Mo 98%
	10% D2EHPA and 5% TBP pH 2.3 (V, Fe, Ca, Mg, Na, K, As, Si, P)	V 95.94%	15% H_2SO_4	V 99.14%

that the acid leaching solution was pretreated with Na_2SO_3 to reduce Fe (III) to Fe (II) and the Al (III) and Mg (II) concentrations should be lower than 10 g/L for avoiding co-extraction. By considering the stripping efficiency and free sulfuric acid in the strip solution, 1.5 M H_2SO_4 solution was found to be the optimum condition for vanadium stripping from the loaded organic. The stripping solution contained a small amount of impurities which would not affect the following precipitation of vanadium.

A summary of the extraction and stripping of molybdenum and vanadium from acid leaching solution of spent catalyst using solvent extraction and a general schematic process flow sheet for the recovery of valuable metals from spent catalysts are shown in Table 2 and Fig. 1, respectively.

5. Summary

Solvent extraction has been employed to recover molybdenum and vanadium from acid leaching solutions of spent catalyst. The extraction behavior of molybdenum and vanadium from acid leaching solution of spent catalysts by four types of extractants has been reviewed: cationic, anionic, neutral and a mixture of cationic and neutral extractants. Neutral extractants can separate molybdenum from cobalt, vanadium and aluminum at high HCl solution but not much investigation has been reported in the separation of molybdenum from vanadium. With cationic and anionic extractants, separation of molybdenum and vanadium from other impurity metals was achieved. However, some problems may be en-

countered when a solvent extraction plant was operated, including emulsification of organic phase, the formation of third phase and appearance of precipitates. It was indicated that a mixture of cationic and neutral extractants had the advantage of being free from the formation of an emulsion and of a third phase, especially from the formation of precipitates in loaded organic. The synergistic solvent extraction system consisting of Cyanex 272, D2EHPA and TBP was favorable for the recovery of molybdenum and vanadium, respectively. Moreover, molybdenum and vanadium from these loaded organic was stripped easily by using ammonia and sulfuric solution, respectively. Consequently, use of a mixture of cationic and neutral extractants is promising for the effective separation and recovery of molybdenum and vanadium from acidic leach solution, in particular from sulfate leach liquor of spent catalyst.

감사의 글

본 논문은 환경부 “환경융합신기술개발사업”의 연구비 지원에 의해 수행되었습니다.

References

1. Park, H.K., Kim, I.H., Parhi, K.P., 2010: Recovery of molybdenum from spent catalyst leach solutions by solvent extraction with Lix 84-I, Sep. Purif. Technol., 74, pp. 294-299.
2. Park, K.H., Mohapatra, D., Reddy, B.R., Nam, C.W., 2006: Hydrometallurgical processing and recovery of molybdenum trioxide from spent catalyst, Int. J. Miner. Process, 80, pp. 261-265.
3. Zeng, L., Cheng, C.Y., 2009: A literature review of the recovery of molybdenum and vanadium from spent hydrodesulphurisation catalyst. Part I: Metallurgical processes, Hydrometallurgy, 98, pp. 1-9.
4. Zeng, L., Cheng, C.Y., 2009: A literature review of the recovery of molybdenum and vanadium from spent hydrodesulphurisation catalysts Part II: Separation and purification and references within, Hydrometallurgy, 98, pp. 10-20.
5. Suzuki and Gao,S.L., 1982: Recovery of valuable metals in spent heavy oil hydrodesulphurization catalyst, Papanese Pat. No. 570882122.
6. Mihashi, T., Motomura, H., 1982: Recovering process of valuable metals from spent petroleum hydrodesulphurization catalysts, Janaese Pat. No 57022119.
7. Siemens, R.E., Jong, B.W., Russel, J.H., 1986: Potential of spent catalyst as a source of critical metals, Conserv. Recycling, 9, pp. 89-96.
8. Mishra, D., Chaudhury, G.R., Kim, D.J., Ahn, J.G., 2010: Recovery of metal values from spent petroleum catalyst using leaching-solvent extraction technique, Hydrometallurgy, 101, pp. 35-40.
9. Barik, S.P., Park, K.H., Parhi, P.K., Park, J.T., 2012: Direct leaching of molybdenum and cobalt from spent hydrodesulphurization catalyst with sulphuric acid, Hydrometallurgy, 111-112, pp. 46-51.
10. Barik, S.P., Park, K.H., Parhi, P.K., Park, J.T., Nam, C.W., 2012: Extraction of metal values from waste spent petroleum catalyst using acidic solutions, Sep. Purif. Technol., 101, pp. 85-90.
11. Ognyanova, A., Ozturk, A.T., Michelis, I.D., Ferella, F., Taglieri, G., Akcil, A., Vegliò, F., 2009: Metal extraction from spent sulfuric acid catalyst through alkaline and acidic leaching, Hydrometallurgy, 100, pp. 20-28.
12. Chen, X.Y., Lan, X.Z., Zhang, Q.L., Ma, H.Z., Zhou, J., 2010: Leaching vanadium by high concentration sulfuric acid from stone coal, Trans. Nonferrous Met. Soc. China, 20, pp. 123-126.
13. Ward, V.C., 1989: Meeting environmental standards when recovering metals from spent catalyst, JOM, 41, pp. 54-55.
14. Sefton, V.B., Fox, R., Lorenz, W.P., 1989: Recovery and separation of metals values from spent hydrodesulphurization catalyst, US Pat. No. 4861565.
15. Banda, R., Nguyen, T.H., Sohn, S.H., Lee, M.S., 2013: Recovery of valuable metals and regeneration of acid from the leaching solution of spent HDS catalysts by solvent extraction, Hydrometallurgy, 133, pp. 161-167.
16. El-Nadi, Y.A., Awwad, N.S., Nayl, A.A., 2009: A comparative study of vanadium extraction by Aliquat-336 from acidic and alkaline media with application to spent catalyst, Int. J. Miner. Process, 90, pp. 115-120.
17. Banda, R., Sohn, S.H., Lee, M.S., 2012: Process development for the separation and recovery of Mo and Co from chloride leach liquors of petroleum refining catalyst by solvent extraction, J. Hazard. Mater., 213-214, pp. 1-6.
18. Nekovář, P., Schrötterová, D., 2000: Extraction of V(V), Mo(VI) and W(VI) polynuclear species by JMT, Chem. Eng. J., 79, pp. 229-233.
19. Lozano, L.J., Juan, D., 2001: Solvent extraction of polyvanadates from sulphate solutions by primene 81R. Its application to the recovery of vanadium from spent sulphuric acid catalysts leaching solutions, Solvent Extr. Ion Exc., 19, pp. 359-676.
20. Li, W., Zhang, Y., Liu, T., Huang, J., Wang, Y., 2013: Comparison of ion exchange and solvent extraction in recovering vanadium from sulfuric acid leach solutions of stone coal, Hydrometallurgy, 131-132, pp. 1-7.
21. Chagnes, A., Rager, M.N., Courtaud, B., Thiry, J., Cote, G., 2010: Speciation of vanadium (V) extracted from acidic sulfate media by trioctylamine in n-dodecane modified with 1-tridecanol, Hydrometallurgy, 104, pp. 20-24.
22. Saberyan, K., Maragheh, M.G., Astari, P., Alamdari, S.K.,

2003: Liquid-liquid extraction of molybdenum(VI) acidic media with Cyanex – 301, Miner. Eng., 16, pp. 391-393.
23. Sato, T., Watanabe, H., Suzuki, H., 1986: Liquid-liquid extraction of molybdenum(VI) from aqueous acid solutions by high-molecular weight amines, Solvent Extr. Ion Exc., 4, pp. 987-998.
24. Bal, Y., Bal, K.E., Cote, G., Lallam, A., 2004: Characterization of the solid third phasaes that precipitate from the organic solutions of Aliquat 336 after extraction of molybdenum(VI) and vanadium(V), Hydrometallurgy, 75, pp. 123-134.
25. Sato, T., Nakamura, T., S., Kawamura, M., 1973: The extraction of vanadium(IV) from hydrochloric acid solutions by di-(2-ethylhexyl)-phosphoric acid, J.inorg. nucl. Chem., 40, pp. 853-856.
26. Sato, T., Ikoma, S., Nakamura, T., 1977: The extraction of vanadium(IV) from hydrochloric acid solutions by long – chain alkyl amine and alkyl ammonium compound, J.inorg. nucl. Chem., 39, pp. 395-399.
27. Sato, T., Ikoma, S., Nakamura, T., 1980: Solvent extraction of vanadium(IV) from hydrochloric acid solutions by neutral organophosphorus, Hydrometallurgy, 6, pp. 13-23.
28. Li, X.B., Wei, C., Wu, J., Li, C.X., Li, M.T., Deng, Z.G., Xu, H.S., 2012: Thermodynamics and mechanism of vanadium(IV) extraction from sulphate medium with D2EHPA, EHEHPA and CYANEX 272 in kerosene, Trans. Nonferrous Met. Soc. China, 22, pp. 461-466.
29. Zhang, P., Inoue, K., Yoshizuka, K., Tsuyama, H., 1996: Extraction and selective stripping of molybdenum(VI) and vanadium(IV) from sulfuric acid solution containing aluminum(III), cobalt(II), nickel(II) and iron(III) by LIX 63 in Exxsol D80, Hydrometallurgy, 41, pp. 45-53.
30. Zeng, L., Cheng, C.Y., 2010: Recovery of molybdenum and vanadium from synthetic sulphuric acid leach solutions of spent hydrodesulphurization catalysts using extraction, Hydrometallurgy, 101, pp. 141-147.
31. Zhang, P., Inoue, K., Yoshizuka, K., Isuyama, H., 1997: A new solvent extraction process for recovery of rare metals from spent hydrodesulfurization catalysts, Kagaku kôgaku ronbunshû, 23, n1, pp.1-10
32. Li, X., Wei, C., Wu, J., Li, M., Deng, Z., Li, C., Xu, H., 2012: Co-extraction and selective stripping of vanadium (IV) and molybdenum (VI) from sulphuric acid solution using 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester, Sep. Purif. Technol., 86, pp. 64-69.
33. Wu, J., Wei, C., Li, X., Wang, S., Wang, M., Li, C., 2012: Selective extraction of Mo using Cyanex-272 and tributyl phosphate from low grade Ni-Mo ore leach liquor, Sep. Purif. Technol., 99, pp. 120-126.
34. Olazabal, M.A., Orive, M.M., Fernandez, L.A., Madariaga, J.M., 1992: Selective extraction of vanadium (V) from solutions containing molybdenum (VI) by ammonium salts dissolved in toluene, Solvent Extr. Ion Exc., 10 (4), pp. 623-635.
35. Valverde Jr, I.M., Paulino, J.F., Afonso, J.C., 2008: Hydrometallurgy route to recover molybdenum, nickel, cobalt and aluminum from spent hydrotreating catalysts in sulphuric acid medium, J. Hazad. Mater., 160, pp. 310-317.
36. Parhi, P.K., Park, K.H., Kim, H.I., Park, J.T., 2011: Recovery of molybdenum from the sea nodule leach liquor by solvent extraction using Alamine 304-I, Hydrometallurgy, 105, pp. 195-200.
37. Gerhardt, N.I., Oalant, A.A., Petrova, V.A., Tagirov, R.K., 2001: Solvent extraction of molybdenum(VI), tungsten (VI) and rhenium(VII) by diisododecylamine from leach liquors, Hydrometallurgy, 60, pp. 1-5.
38. Li, X., Wei, C., Deng, Z., Li, M., Li, C., Fan, G., 2011: Selective solvent extraction of vanadium over iron from a stone coal/ back shale acid leach solution by D2EHPA/ TBP, Hydrometallurgy 105, pp. 359-363.
39. Li, C.X., Wei, C., Deng, Z.G., Li, M.T., Li, X.B., Fan, G., 2010: Recovery of vanadium from black shale, Tran. Nonferrous Met. Soc. China, 20, pp. 127-131.
40. Deng, Z.G., Wei, C., Fan, G., Li, M.T., Li, C.X., Li, X.B., 2010: Extracting vanadium from stone-coal by oxygen pressure acid leaching and solvent extraction, Tran. Nonferrous Met. Soc. China, 20, pp. 118-122.

응우엔 티홍

• 깐터대학교 (베트남) 물리교육학과 학사
• 깐터대학교 (베트남) 물리학 강사
• 현재 목포대학교 신소재공학과 석사

李 晩 承

• 현재 목포대학교 신소재공학과 교수
• 당 학회지 제11권 1호 참조