

SCR 폐촉매 침출액으로부터 습식제련법에 의한 바나듐, 텅스텐의 회수#

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Recovery of the Vanadium and Tungsten from Spent SCR Catalyst Leach Solutions by Hydrometallurgical Methods#

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요 약

2000년대에 접어들면서 선택적 촉매 환원(SCR) 촉매에 대한 광범위한 수요가 점차 증가하고 있다. SCR 촉매는 환경보호를 위해 질소산화물(NO_x)의 배출 방지에 사용 된다. 일반적으로 SCR 촉매의 주성분은 TiO₂(70~80%), WO₃(7~10%), V₂O₅(~1%) 등으로 구성되어 있었다. SCR 폐촉매는 대개 매립되어 폐기 되는데, 분해도가 극히 낮아 매립지에 영구적으로 남아있게 된다는 문제점을 가지고 있다. 따라서 환경을 보호하고 폐촉매에 함유되어 있는 유가금속의 회수를 위하여 새로운 침단기술의 개발이 필요하다. 이러한 SCR 폐촉매의 처리를 위해 침출 및 액-액 추출과 같은 습식제련법이 설계되고 개발되었다. 첫 번째 단계에서 SCR 폐촉매로부터 바나듐과 텅스텐을 선택적으로 침출한 후, 액-액 추출 공정에 의해 처리되었다. 바나듐과 텅스텐의 선택적 추출을 위해 D2EHPA, PC 88A, TBP, Cyanex 272, Aliquat 336과 같은 다양한 상용 용매추출제를 이용한 실험을 수행하였다. 바나듐과 텅스텐의 추출 및 분리를 위해 세정(scrubbing) 및 탈거(stripping) 연구가 수행되고 최적화 되었다. 3상의 생성을 억제하기 위해 iso-decanol 시약을 사용하여 최적화 하였다.

주제어 : 회수, 바나듐, 텅스텐, 습식제련, SCR 폐촉매

Abstract

In new millennium, wide-reaching demands for selective catalytic reduction (SCR) catalyst have been increased gradually in new millennium. SCR catalyst can prevent the NO_x emission to protect the environment. In SCR catalyst the main composition of the catalyst is typically TiO₂ (70~80%), WO₃ (7~10%), V₂O₅ (~1%) and others. When the SCR catalysts are used up and disposed to landfills, it is problematic that those should exist in the landfill site permanently due to their extremely low degradability. A new advanced technology needs to be developed primarily to protect environment and then recover the valuable metals. Hydrometallurgical techniques such as leaching and liquid-liquid extraction was designed and developed for

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the spent SCR catalyst processing. In a first stage, V and W selectively leached from spent SCR catalyst, then both the metals were processed by liquid-liquid extraction process. Various commercial extractants such as D2EHPA, PC 88A, TBP, Cyanex 272, Aliquat 336 were tested for selective extraction of title metals. Scrubbing and stripping studies were tested and optimized for vanadium and tungsten extraction and possible separation. 3rd phase studies were optimized by using iso-decanol reagent.

Key words : recovery, vanadium, tungsten, hydrometallurgy, spent SCR catalyst

1. Introduction

Selective catalytic reduction (SCR) catalysts were used to control the NO_x reagents in air. These NO_x reagents are the cause for air pollution. Mainly NO_x reagents will generate from coal power plants. Due to strict environmental regulations implementation in Korea, all of the coal power plants are utilizing the SCR catalyst to prevent the NO_x pollution¹⁻³.

In new millennium, universal demand for SCR catalyst has been increased progressively due to strengthening environmental regulatory for NO_x emission from stationary and mobile applications. In an effort to develop a better SCR catalyst, it is considered that V₂O₅-WO₃/TiO₂ catalyst is the most effective and widely employed to reduce NO_x emissions.

Many methods were applied and developed for spent catalyst processing to recover the valuable metals, successfully in reported literature⁴⁻¹².

V₂O₅-WO₃/TiO₂ catalyst having properties such as its high NO_x conversion efficiency, durability from poisons and thermal, sulfur resistance, and wide operation temperature window has been considered to be the most commercial and excellent NO_x conversion efficiency.

Our ongoing research on spent SCR catalyst processing, we have been developed the soda-roasting followed by water leaching, alkali leaching, pressure leaching were reported, recently¹³⁻¹⁶.

The present study feed stock was collected from Samcheonpo thermoelectric power plant, Korea and the spent SCR catalyst structure was honeycomb. This is V₂O₅-WO₃/TiO₂ type catalyst. After pretreatment roasting, spent SCR catalyst was dissolved by alkali. The generated

leach liquor was followed by solvent extraction processing for vanadium and tungsten possible separation and metal loading enrichment.

2. Experimental

iCAP 6000 Series, Thermo Scientific, USA ICP-OES are used for metal ion analysis. Aqueous feed solutions were generated from alkali fusion of spent SCR catalyst followed by water leaching process.

In the alkali fusion, Na₂CO₃ (99.8%, Kanto Chemicals Co., Inc., Japan) was used as an alkali fusion agent for the soda-melting reactions. Before it used, further dehydration of Na₂CO₃ was not conducted. Mixing ratio of the spent SCR catalyst and Na₂CO₃ was 1 : 1.2 by weight (MO_x/MO_x+Na₂O = 0.5, where M = Ti, Si, W, and V). Temperature of soda-melting reactions was set up to 1000°C. Dense alumina crucible was use for alkali fusion reactions. Alkali fused melt dropped from the crucible was cooled and then pulverized. Before the water leaching of alkali fusion product, solidified alkali fusion melts (bulk) was grinded using a pin mill. Particle size distribution of pulverized soda melts was mainly ranging from 1 to 200 μm.

Water leaching of alkali fusion product was conducted under following conditions: temperature, 80°C; S/L (Weight of solid / Volume of liquid) ratio, 0.2; leaching time, 1 h; stirring speed, 350 rpm. During the water leaching, vaporized water was collected by water-cooled condenser. Water leaching slurry was filtrated and separated into solution and residue by vacuum filtration. In the further process, filtrated water leaching solution was used as feed solution in solvent extraction process.

The physical appearance of the spent SCR catalyst was presented in Fig. 1. It majorly contains 70.9 wt% of TiO_2 , 7.73 wt% of WO_3 and 1.23 wt% of V_2O_5 etc. After pulverization of the spent SCR catalyst, EDS-SEM analysis was carryout and pictures were presented in Fig. 2.

The present study leach liquor obtained from spent SCR catalyst and initially it is having 1238 mg/L of vanadium and 8635 mg/L of tungsten at pH of the liquor was 14. Further studies diluted with mineral acids such as HCl and H_2SO_4 to reach lower pH conditions. Each experiment analyzed the fresh feed solution and applied for data analysis.

Aliquat 336 received from Cognis, Ireland was used as such. D2EHPA and TBP received from Aldrich and PC 88A received from Daihachi Chemicals Japan were used as such. All other chemicals were Analar grade.

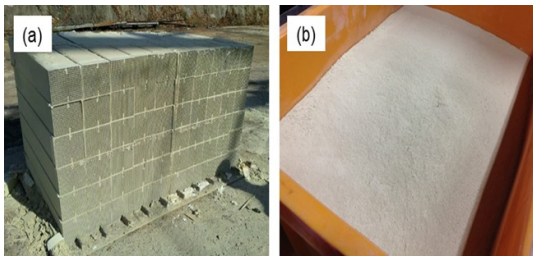


Fig. 1. Actual appearance of spent $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalyst module, (a), and its pulverized sample, (b).

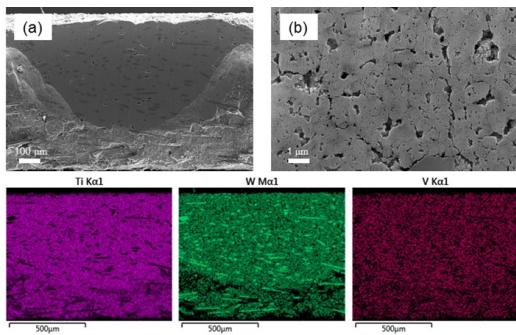


Fig. 2. EDS-SEM analysis results for the vertical plane of spent $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalyst: (a) detected plane, (b) morphology of vertical plane, and distribution of titanium, tungsten, and vanadium.

Solvent extraction experiments were carried by contacting aqueous and organic phases in separating funnels and shake by mechanical incubator at room temperature. After experiment, metals in aqueous solution were analyzed to determine distribution coefficient (D_E) and percentage extraction (% E) values.

$$\text{Extraction, } D_E = \frac{[M]_{\text{in organic phase}}}{[M]_{\text{in aqueous phase}}} \quad (1)$$

$$\% \text{Extraction} = D_E \times 100 / (D_E + 1) \quad (2)$$

$$\text{Stripping or scrubbing, } D_s = \frac{[M]_{\text{in aqueous phase}}}{[M]_{\text{in organic phase}}} \quad (3)$$

$$\% \text{Stripping or } \% \text{scrubbing} = D_s \times 100 / (D_s + 1) \quad (4)$$

3. Results and discussions

3.1. Selection of extractant system

Various phosphorous and nitrogen based extractants were utilized for better extraction and possible separation of the tungsten and vanadium from spent SCR leach liquors. Three initial pH conditions were tested and obtained data were presented in Figs. 3 to 5. The results make known that; higher pH condition is not good for

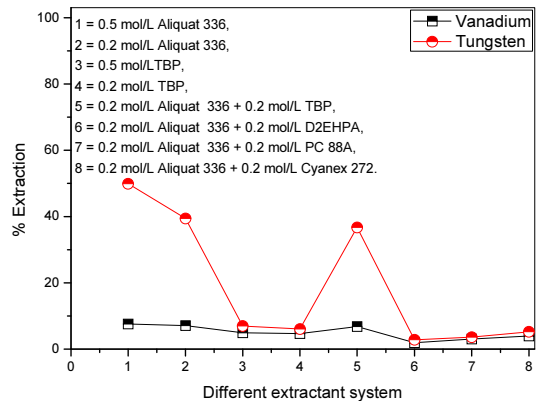


Fig. 3. Effect of different extractant systems on vanadium and tungsten extraction from spent SCR catalyst leach solutions at initial pH 14 and equilibrium pH 13.5.

extraction of both metals (less than 10% extracted). The other pH conditions 7.6 to 10 are good for to achieve quantitative extraction of both the metals. And this study further indicated that, nitrogen based extractants were

better than phosphorous based extractants. Further experiments the aqueous pH solutions were good have initial >10. And nitrogen based extractants were chosen for further studies.

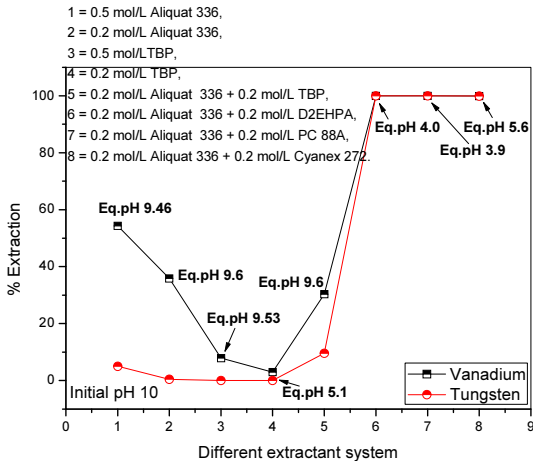


Fig. 4. Effect of different extractant systems on vanadium and tungsten extraction from spent SCR catalyst leach solutions at initial pH 10.

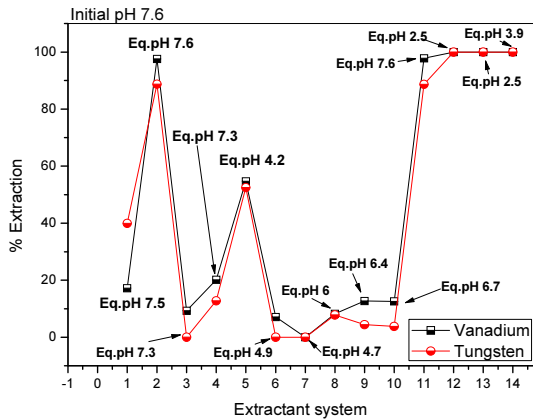


Fig. 5. Effect of different extractant systems on vanadium and tungsten extraction from spent SCR catalyst leach solutions at initial pH 7.6 (1 = 0.5 mol/L Aliquat 336, 2 = 0.2 mol/L Aliquat 336, 3 = 0.5 mol/L TBP, 4 = 0.2 mol/L TBP, 5 = 0.5 mol/L D2EHPA, 6 = 0.2 mol/L D2EHPA, 7 = 0.5 mol/L PC 88A, 8 = 0.2 mol/L PC 88A, 9 = 0.5 mol/L Cyanex 272, 10 = 0.2 mol/L Cyanex 272, 11 = 0.2 mol/L Aliquat 336 + 0.2 mol/L TBP, 12 = 0.2 mol/L Aliquat 336 + 0.2 mol/L D2EHPA, 13 = 0.2 mol/L Aliquat 336 + 0.2 mol/L PC 88A, 14 = 0.2 mol/L Aliquat 336 + 0.2 mol/L Cyanex 272).

3.2. Effect of commercial based extractants

Based on previous experiments nitrogen based extractants were used for further study. For comparison purpose

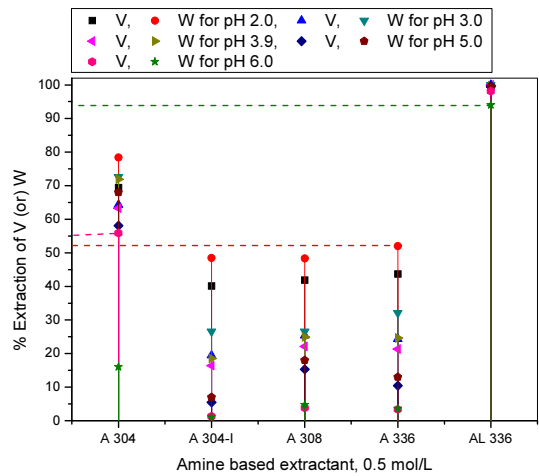


Fig. 6. Amine based extractants influence on vanadium and tungsten extraction from spent SCR catalyst leach liquors (A 304 = Alamine 304, A 304-I = Alamine 304-I, A 308 = Alamine 308, A 336 = Alamine 336, AL 336 = Aliquat 336).

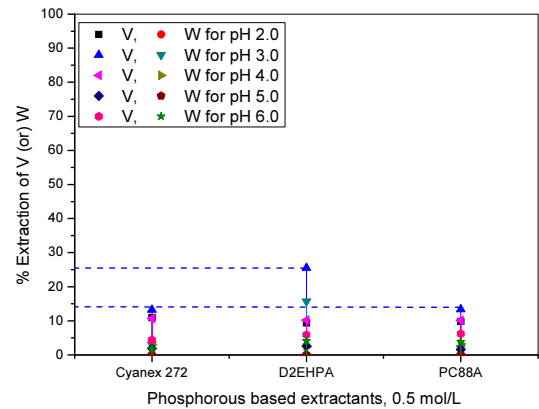


Fig. 7. Phosphorous based extractants influence on vanadium and tungsten extraction from spent SCR catalyst leach liquors.

phosphorous based extractants are also studied. Extractants influence with pH varied from 2 to 6 for vanadium tungsten extraction from spent SCR catalyst. The gained experimental results were presented in Figs. 6 and 7. Amines are proved that, better than phosphorous based extractants for vanadium and tungsten extraction and possible separation process. The results reveals that, the extraction efficiencies were as follows the order: Aliquat 336 > Alamine 304 > Alamine 336 > Alamine 308 > Alamine 304-I.

3.3. Third phase studies

Among the all amine based extractants Aliquat 336 proved the better extraction capabilities for vanadium and tungsten. But it forms third phase, to remove third phase, this study needs to apply modifier. Two different type of the phase modifiers such as tri-butyl-phosphate (TBP) and iso-decanol (IDA) were used (Tables 1 and 2). Both the phase modifiers were suitable for to remove the third phase but the extraction efficiency was reduced ~30 to 35%.

Table 1. 0.5 mol/L Aliquat + 10% TBP used as a modifier

Element	Feed, mg/L	Raf. Aq, mg/L	LO, mg/L	D	% Extr.	SF = D_V/D_W
Vanadium	887	303	584	1.927	65.8	1.25
Tungsten	8252	3250	5002	1.539	60.6	

Table 2. 0.5 mol/L Aliquat + 10% IDA used as a modifier

Element	Feed, mg/L	Raf. Aq, mg/L	LO, mg/L	D	% Extr.	SF = D_V/D_W
Vanadium	887	270	617	2.285	69.6	1.27
Tungsten	8252	2950	5302	1.797	64.3	

3.4. Water washings of the loaded organic

After extraction experiment, the loaded organic (LO) phase was washed with distilled water. To possible to remove the un-wanted metals from LO and the gained data was presented in Tables 3 and 4. The extraction LOs were used for 3rd phase studies (LO data from Tables 1 and 2) and both the LOs after water washings loss nominal loss of tungsten and vanadium.

Table 3. Water washing of the loaded organic generated by 0.5 mol/L Aliquat 336 + 10% of TBP

Element	0.5 mol/L of AL 336 + 10% TBP LO, mg/L	Raf. Aq, mg/L	RLO1, mg/L
Vanadium	584	3	581
Tungsten	5002	41	4961

Table 4. Water washing of the loaded organic generated by 0.5 mol/L Aliquat 336 + 10% of IDA

Element	0.5 M of AL 336 LO, mg/L	Raf. Aq, mg/L	RLO1, mg/L
Vanadium	617	>2	615
Tungsten	5302	24	5278

3.5. Scrubbing studies

Scrubbing studies are made for possible separation of co-extracted metal. Present study acidified water (pH 1.7, acidified low diluted hydrochloric acid). The results are shown that (Tables 5 and 6), LO of 0.5 mol/L Aliquat + 10% TBP performed better removal of vanadium than LO of 0.5 mol/L Aliquat + 10% IDA (here both the metals are scrubbed).

Table 5. Scrubbing with acidified water pH 1.7, LO generated by 0.5 mol/L Aliquat + 10% TBP

Element	RLO1, mg/L	Raf. Aq, mg/L	RLO2, mg/L
Vanadium	581	112	469
Tungsten	4961	10	4951

Table 6. Scrubbing with acidified water pH 1.7, LO generated by 0.5 mol/L Aliquat + 10% IDA

Element	RLO1, mg/L	Raf. Aq, mg/L	RLO2, mg/L
Vanadium	615	163	452
Tungsten	5278	142	5136

3.6. Stripping studies

Finally, the loaded metals were recovered with same acidified water pH 1.7 used for vanadium and tungsten. Both the metals more than 90% were recovered (Tables 7 and 8).

Table 7. Stripping with acidified water pH 1.7, LO generated by 0.5 mol/L Aliquat 336 + 10% of TBP processing

Element	RLO2, mg/L	Raf. Aq, mg/L	RLO3, mg/L
Vanadium	469	27	442
Tungsten	4951	68	4883

Table 8. Stripping with acidified water pH 1.7, LO generated by 0.5 mol/L Aliquat 336 + 10% of IDA processing

Element	RLO2, mg/L	Raf. Aq, mg/L	RLO3, mg/L
Vanadium	452	19	433
Tungsten	5136	47	2089

4. Conclusions

The present study concludes that, both the title metals such as vanadium and tungsten were positively extracted 60 to 65% from spent SCR catalyst leach liquors by using Aliquat 336 as an extractant system and kerosene use as a diluent. Water washings, scrubbing and stripping studies were developed and effectively up to 90% of vanadium and tungsten metals were recovered. This study reveals that, need to develop future work on metal enrichment as well as possible separation each other of vanadium and tungsten from spent SCR catalyst leach liquors.

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