

SCR 폐촉매 침출액으로부터 용매추출법에 의한 유가금속의 추출[#]

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Spent SCR Catalyst Leach Liquor Processed for Valuable Metals Extraction by Solvent Extraction Technique[#]

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요 약

선택적 촉매 환원법(SCR)은 여러 산업에서 질소산화물(NOx)에 의한 대기오염을 줄일 수 있는 매우 유망한 기술이다. SCR 촉매의 소비는 기술이 발전함에 따라 매년 증가하고 있지만, 촉매의 수명은 제한되어 있으며, 일반적으로 수명이 다해 활성이 떨어진 폐촉매는 재활용 되지 않고 매립되어 처리되고 있다. 현재 가장 널리 사용되는 촉매는 V₂O₅-WO₃/TiO₂로 구성되어 있으며, 약 5%_{wt}의 V₂O₅와 7-10%_{wt}의 WO₃를 함유하고 있다. 본 연구는 2차 공급원으로부터 유용 금속을 회수할 수 있는 기술개발에 대한 전세계적인 관심과, 다양한 분야에서의 바나듐 및 텅스텐의 수요에 대한 안정적인 공급을 대비하기 위한 기술개발을 바탕으로 한다. 추출 시간, pH 의존도 및 추출 농도에 대한 연구는 희석제 exsol D80에 추출제로 Aliquat 336을 사용하여 수행되었다. 두 금속의 최적 추출을 위한 조건은 약산성(~5.0) 영역에서 0.5mol/L의 Aliquat 336을 함유한 유기상과 30분 동안 추출 반응을 수행해야 하는 것으로 확인되었다. 또한 counter-McCabe-Thiele 분석으로부터 99%의 바나듐을 제거하기 위해 1단의 단수가 필요하고, 텅스텐의 추출을 위해 2단의 단수가 필요하였으며, 향류추출공정(counter-current simulations) 방식을 통한 이론적 접근의 적합성을 증명하였다.

주제어 : SCR 촉매, 바나듐, 텅스텐, 용매추출

Abstract

Selective catalytic reduction (SCR) has been a promising technology to reduce the air pollution caused by nitrogen oxides (NOx) in several industries. The consumption of SCR catalysts increases every year as technology evolves, however those have a limited lifespan and usually end up in landfills after they deactivate. Currently, the most widely used catalyst for and stationary applications is V₂O₅-WO₃/TiO₂ which can contain around 50% wt V₂O₅ and 7-10% wt of WO₃. The vast uses for both vanadium

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and tungsten and the worldwide interest in recycling methods that allow for the extraction of metals from secondary sources represent the major motivation for this research. The extraction time, pH dependency, extraction concentration studies were carried out using Aliquat 336 in exsol D80 as the extractant. It was determined that to optimize the extraction of both metals 30min of contact time with an organic phase containing 0.5mol/L of Aliquat 336 are needed at a slightly acidic pH (~5.0). In addition, counter McCabe-Thiele studies allowed us to determine that one stage is necessary for the removal of 99% of vanadium while 2 stages are necessary for the extraction of tungsten and counter current simulations proved that the theoretical approach was correct.

Key words : SCR catalyst, vanadium, tungsten, solvent extraction

1. Introduction

In the last decades, various secondary wastes has been used as source of different metals due to the rapid depletion of ores and the increased interest in green alternatives to supply the increasing demand of the same^{1,2}). Among those sources, sludges, spent catalysts, scraps and e-waste have played a major role in the supply chain of strategic as well as base metals such as vanadium and tungsten³⁻⁶). Coupled with the green technology approach as well as the stricter regulations for emissions in stationary and mobile sources, selective catalytic reduction (SCR) has been proven as the primary method used for the reduction of nitrogen oxides (NO_x) emitted to the environment causing air pollution⁷). Currently, the most used SCR catalyst for stationary and vehicle application is the V₂O₅-WO₃ in TiO₂ matrix which can contain around 0.5-1% wt V₂O₅ and 7-10% wt of WO₃⁸⁻¹¹). Even tough, this catalyst offers great durability and regeneration capacity it has a limited chemical lifespan (roughly 3-6 years), after which it will end up most probably in landfills, becoming a major source of contamination, due to the toxicity of vanadium compounds^{8,9}). The increasing demand of SCR catalyst has created a big niche for secondary resources of vanadium and tungsten, which could be recovered and reutilized.

During a previous study conducted in our research laboratory, the selective leaching of titanium was conducted, while leaving a soda roasted liquor containing approximately 7000mg/L of tungsten and 600mg/L of

vanadium, which cannot be easily separated due to their similar chemical and physical properties^{9,12-14}).

In the present work, leach liquor obtained from SCR spent catalyst is used as the source of vanadium and tungsten recovery using solvent extraction. Various authors have reported different hydrometallurgical routes to extract vanadium and tungsten from different secondary sources, however there is no available study that successfully extracts and enriches these metals from a high concentration liquor. In addition, the extractant used is a quaternary amine, the commercial extractant Aliquat 336 which is well known as a green ionic liquid (IL) reported for the extraction of several base and strategic metals^{15,16}). Based on this study it would be possible to determine the optimum parameters for both metal enrichment and recovery.

2. Experimental

2.1. Materials and Method

The leach liquor used for this study was provided from a previous work of our research group⁹), which was made using a honeycomb spent catalyst from the Samcheonpo thermoelectric power plant in South Korea and contains around 600mg/L of vanadium and 7000mg/L of tungsten. For the extraction experiments, Aldrich Aliquat 336 was used as received and Exsol D80 (non aromatic) was used as a diluent for every experiment and taken without further purification. The solvent extraction investigation was carried out in a 125 ml volumetric flask mounted over incubated Shaker (SI-300/300R/600/

600R). In each of the experimental study, equi-volume (unless otherwise specified) of aqueous and organic solution was contacted for 30 minutes to attain the equilibrium. After the phase disengagement, either of the phases were separated out and read for determination of the W/V concentration. The aqueous phase was analyzed by ICP-OES after making suitable dilution. All the experiments are performed under ambient temperature ($\pm 25^\circ\text{C}$). The extraction efficiency was determined based upon the equations as follows.

$$D = \frac{[M_{\text{organic phase}}]}{[M_{\text{aqueous phase}}]} \quad (1)$$

Where, M represents vanadium or tungsten.

$$\%E = \frac{D * 100}{D + 1} \quad (2)$$

2.2. Analysis

Chemical analysis of the aqueous phase to determine the content of vanadium and tungsten (before and after extraction) was conducted using an inductively coupled plasma optical emission spectrometer (ICP-OES, iCAP Duo6300, Thermo Scientific, UK).

3. Results

3.1. Time experiment

The pH of leach liquor used for the extraction was adjusted using hydrochloric acid until initial pH 7 and contacted in 125ml separating funnels with the same volume of the organic phase composed of 20ml of aliquat 336 0.5mol/L. The contact times were varied from 1 min to 120min to determine when the extraction equilibrium is attained.

Fig. 1 shows how the percentage of the extraction changes in time and it is observed that around 30min the percentage of extraction reaches a plateau zone were increasing the time would have no influence on the

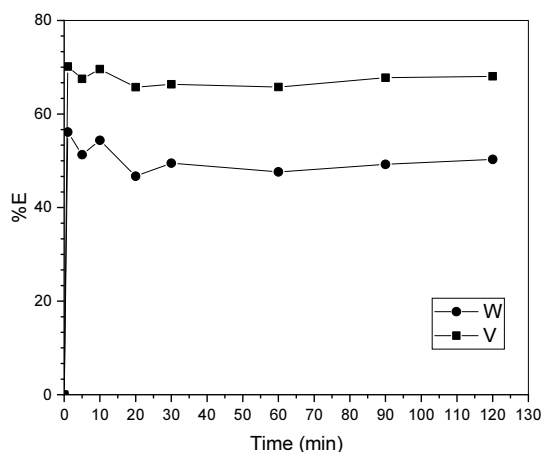


Fig. 1. Variation of percentage of extraction in time.

extraction capability of the process. For further studies in this paper, 30 minutes will be used as the extraction time unless specified. As can be seen from the results, after 30min of contact time the extraction of vanadium reaches an approximate of 65% while tungsten reaches 44% of extraction.

3.2. pH and extractant concentration optimization

The effect of extractant concentration for in the vanadium and tungsten extract ion were investigated. For 20 ml aqueous samples (initial pH 7 adjusted with HCl), the concentration of extractant was varied from 0.1 mol/L to 1mol/L. The extraction was carried out using an organic/aqueous ratio of one for 30 min in a wrist shaker at 250rpm.

The extraction efficiency of vanadium and tungsten when aliquat 336 concentration is modified can be seen in Fig. 2. There is a steep increase on the efficiency when concentration of the extractant changes from 0.1 mol/L to 0.5 mol/L, however there is no significant increase in the percentage of extraction above 0.5mol/L of extractant. Since the extraction trend reaches a plateau zone, it was determined that 0.5mol/L will be the concentration of aliquat 336 used for further experiments.

In addition, the distribution coefficient for vanadium and tungsten were studied and plotted against the aliquat

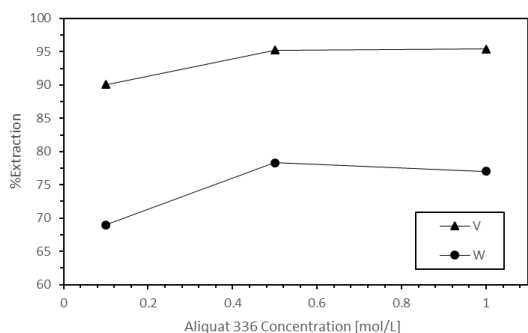


Fig. 2. Effect of extractant concentration in the percentage of extraction.

336 concentration (not shown) giving linear relationships with a slope close to the unity for both metals, which signifies the association of one mole of the extractant during the extraction process. Since, vanadium and tungsten offer a variety of anions in solution, it favors an anion exchange mechanism with Aliquat 336¹⁷⁾.

Equilibrium pH is one of the most important parameters for solvent extraction because it determines the species present in the aqueous phase and the nature of the species will determine if Aliquat 336 can extract them¹⁸⁾. The pH of the leach liquor aqueous solution was varied using HCl from an initial pH of 5.0 to 7.35, while keeping the organic phase constant using Aliquat 336 (A/O=1) in D80 at a concentration of 0.5mol/L during 30 min in a wrist shaker at 250rpm.

Fig. 3 shows that increasing the pH towards an alkaline solution decreases the extraction for both metals and in slightly acid solutions (equilibrium pH ~6) 95% of extraction of vanadium and tungsten can be achieved. In addition, it can be observed that the equilibrium pH (plotted in Fig. 3) is higher than the initial pH for all the experiments done, which indicates the complexation of the whole vanadium or tungsten molecule without the release of any H^+ leading to the increase of the pH of the aqueous phase^{18,19)}.

Finally, the distribution coefficient for vanadium and tungsten were plotted against the equilibrium pH (not shown) giving linear relationships with a slope close to

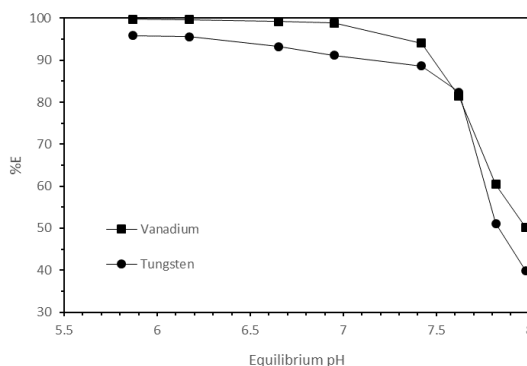
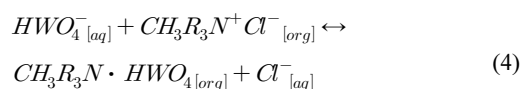
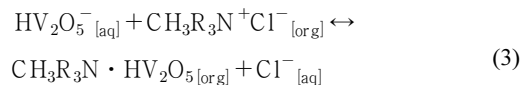


Fig. 3. Influence of the equilibrium pH in the percentage of extraction.

the unity for both metals, which signifies the association of one proton towards the organic phase. From literature it is well known that in slightly acidic media vanadium and tungsten can be present as a series of anionic species¹⁸⁾ including $HV_2O_5^-$ and HWO_4^- which helped for the elucidation of the extraction mechanism as follows.



3.3. Extraction isotherms of tungsten and vanadium

To find out the number of stages and possibility of enriching vanadium and tungsten in the loaded organic phase during extraction, the extraction isotherm for both metals was obtained by contact of the aqueous feed at pH 5 with Aliquat 336 0.5 M at different A/O ratios from 1 to 10 (Fig. 4). From the extraction isotherms it can be observed that for tungsten at a phase ratio A/O=3 almost complete extraction can be done in two-stages, while for vanadium at the same phase ratio a complete loading of the organic phase can be achieved at one stage.

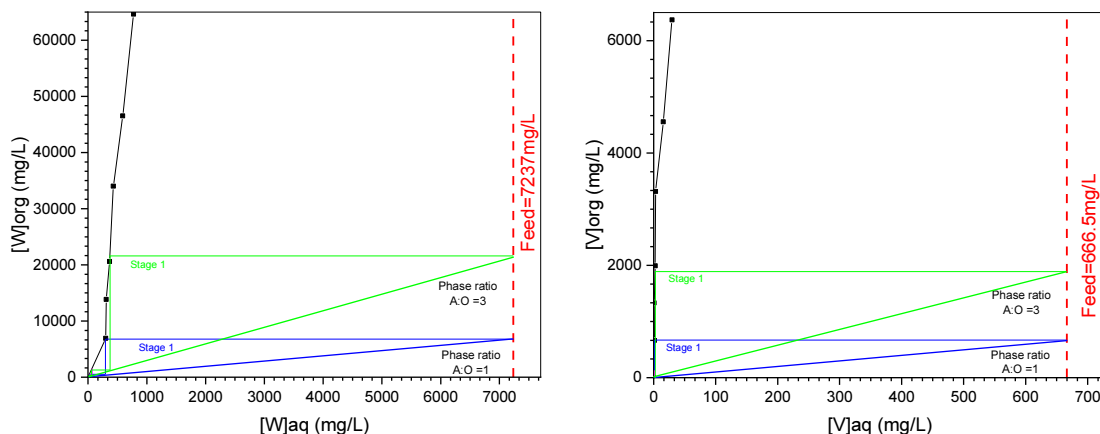


Fig. 4. Extraction isotherms for tungsten and vanadium.

To confirm, the McCabe-Thiele diagram theoretical predictions, counter current extractions were performed at an $A/O = 3$. The results showed a raffinate containing 0.23mg/L of vanadium and 270.2mg/L of tungsten, which corresponds to a 99.95% and 96.07% extraction of vanadium and tungsten. To increase the percentage of extraction for the process, a three-stage counter current extraction was tested and it resulted in a 99.98% extraction of vanadium and 99.11% extraction of tungsten.

4. Conclusion

The extraction of vanadium and tungsten from SCR spent catalyst leach liquor using the quaternary ammonia salt Aliquat 336 in Exxol D80 was studied. The main parameters that affect extraction are time, concentration of extractant and equilibrium pH in the solution. It can be seen that 30 minutes is the optimum time for extraction and was used during the present study. In addition, the equilibrium pH was analyzed in the range of slightly acid ($\text{pH} \sim 6$) to slightly basic ($\text{pH} \sim 8$) and it was determined that slight acidity maximizes the extraction percentage for both metals. Furthermore, increasing the extractant concentration more than 0.5mol/L does not offer a great advantage for the extraction of the desired valuable metals, reason why it was chosen as the

concentration used during the investigation. The extraction isotherms for vanadium and tungsten were determined and for an A/O phase ratio of 3 it can be seen that one stage is enough to reach 99% of extraction in the case of vanadium, however for tungsten at least 2 stages are necessary to reach the desired loading. Counter current extraction tests were performed and 99.9% vanadium and 99% of tungsten were extracted in a three stage counter current process.

In summary, the use of Aliquat 336 in D80 at slightly acidic conditions is an effective mean to extract and recover vanadium and tungsten from SCR spent catalyst. Further studies in stripping are necessary for a total understanding of the extraction and recovery system.

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References

1. Brunner, P.H., 2011 : Urban mining a contribution to reindustrializing the city, *Journal of Industrial Ecology*, 15, pp.339-341.
2. Oh, J.-H., Kim, M.-S., Shin, H.-D., et al., 2007 : A study of the research trends and the material flow on the unrecycled materials in Korea - The current situation of recycling technology for waste resources in Korea, *Journal of the Korean Institute of Resources Recycling*, 16(2), pp.63-76.
3. Kumar, A., Holuszko, M. and Espinosa, D.C.R., 2017 : E-waste: An overview on generation, collection, legislation and recycling practices, *Resources, Conservation and Recycling*, 122, pp.32-42.
4. Kim, J.-H., Seo, G.-M., Yang, J.-K., et al., 1998 : Recovery of molybdenum from the desulfurizing spent catalyst, *Journal of the Korean Institute of Resources Recycling*, 7(2), pp.9-15.
5. Kim, M.-S., Kim, B.-S., Kim, E.-Y., et al., 2011 : Recovery of platinum group metals from the leach solution of spent automotive catalysts by cementation, *Journal of the Korean Institute of Resources Recycling*, 20(4), pp.36-45.
6. Kim, J.-H. and Yang, J.-G., 1995 : Recovery of valuable metals from the desulfurizing spent catalyst used in domestic petrochemical industry, *Journal of the Korean Institute of Resources Recycling*, 4(3), pp.2-9.
7. Kim, J.W., Lee, W.G., Hwang, I.S., et al., 2015 : Recovery of tungsten from spent selective catalytic reduction catalysts by pressure leaching, *Journal of Industrial and Engineering Chemistry*, 28, pp.73-77.
8. Choi, I.H., Moon, G., Lee, J.Y., et al., 2018 : Extraction of tungsten and vanadium from spent selective catalytic reduction catalyst for stationary application by pressure leaching process, *Journal of Cleaner Production*, 197, pp. 163-169.
9. Jyothi, R.K., Moon, G., Kim, H.-R., et al., 2017 : Spent V_2O_5 - WO_3 / TiO_2 catalyst processing for valuable metals by soda roasting-water leaching, *Hydrometallurgy*, 175, pp.292-299.
10. Kim, H.-R., Lee, J.-Y. and Kim, J.-S., 2012 : Leaching of vanadium and tungsten from spent SCR catalysts for De- NO_x by soda roasting and water leaching method, *Journal of the Korean Institute of Resources Recycling*, 21(6), pp.65-73.
11. Huo, Y., Chang, Z., Li, W., et al., 2015 : Reuse and valorization of vanadium and tungsten from waste V_2O_5 - WO_3 / TiO_2 SCR catalyst, *Waste and Biomass Valorization*, 6, pp.159-165.
12. Choi, I. H., Moon, G., Lee, J.Y., et al., 2018 : Hydrometallurgical processing of spent selective catalytic reduction (SCR) catalyst for recovery of tungsten, *Hydrometallurgy*, 178, pp.137-145.
13. Choi, I., 2018 : Study on the recovery of vanadium and tungsten from spent V_2O_5 - WO_3 / TiO_2 Catalyst, University of Science and Technology (UST), Resources Recycling PhD dissertation thesis.
14. Kim, H.I., Moon, G., Choi, I., et al., 2018 : Hydrometallurgical process development for the extraction, separation and recovery of vanadium from spent desulfurization catalyst bio-leach liquors, *Journal of Cleaner Production*, 187, pp.449-458.
15. Wei, W., Reddy, D.H.K., Bediako, J.K., et al., 2016 : Aliquat-336-impregnated alginate capsule as a green sorbent for selective recovery of gold from metal mixtures, *Chemical Engineering Journal*, 289, pp.413-422.
16. Wei, W., Cho, C.W., Kim, S., et al., 2016 : Selective recovery of Au(III), Pt(IV), and Pd(II) from aqueous solutions by liquid-liquid extraction using ionic liquid Aliquat-336, *Journal of Molecular Liquids*, 216, pp.18-24.
17. El-Nadi, Y.A., Awwad, N.S. and Nayl, A.A., 2009 : A comparative study of vanadium extraction by Aliquat-336 from acidic and alkaline media with application to spent catalyst, *International Journal of Mineral Processing*, 92, pp.115-120.
18. Nguyen, T.H. and Lee, M.S., 2016 : A review on the separation of molybdenum, tungsten, and vanadium from leach liquors of diverse resources by solvent extraction, *Geosystem Engineering*, 19(5), pp.247-259.
19. Nakamura, T., Nishihama, S. and Yoshizuka, K., 2009 : A novel extractant based on d-glucosamine for the extraction of molybdenum and tungsten, *Solvent Extraction Research and Development*, 16, pp.47-56.

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