

## Recycling of Tungsten and Vanadium from Spent SCR Catalyst using Different Amine and Phosphorous-based Extractants

ANA BELEN CUEVA-SOLA<sup>1,2</sup>, JONG HYUK JEON<sup>1</sup>, JIN-YOUNG LEE<sup>1,2</sup>, RAJESH KUMAR JYOTHI<sup>1,2\*</sup>

<sup>1</sup>Resources Utilization Research Division, Korea Institute of Geoscience and Mineral Resources (KIGAM), Daejeon 34132, Korea

<sup>2</sup>Department of Resources Engineering, Korea University of Science and Technology (UST), Daejeon 34113, Korea

**Abstract :** Due to the strict regulations in terms of gas effluents from industry the demand of several catalyst has increased greatly; one of them is SCR catalyst, which enables the treatment of noxious NO<sub>x</sub> to be converted into N<sub>2</sub> to be released in the air. As the demand grows, also the dispose of these catalyst becomes a pressing problem, thus the recycling of vanadium and tungsten from the catalyst becomes an opportunity to convert waste to wealth. Various commercial extractants (amine-based and phosphorous-based) are analyzed and solvent extraction conditions optimized for the enrichment of vanadium and tungsten or possible separation of them.

**Keywords:** Solvent Extraction, Amine-Based Extractants, Spent SCR Catalyst, Recycling

### 1. INTRODUCTION :

Selective catalytic reduction has been widely regarded as the best technology to reduce gaseous effluents that contain nitrogen oxides (NO<sub>x</sub>). The term NO<sub>x</sub> refers to NO<sub>2</sub>, NO, N<sub>2</sub>O, however regulations are usually in terms of NO<sub>2</sub> due to the oxidation of NO and the minor amount of effluents of N<sub>2</sub>O [1-3]. The main generation of NO<sub>x</sub> happens in combustion power plants, especially in coal combustion and due to the strict regulations in gas emissions worldwide [4-6]; there is a constantly increasing demand on the SCR catalyst.

SCR catalyst containing 7 to 10% of W, 0.5 to 1.5% V and 70 to 80% Ti are regarded as the most commercial efficient for industry [7,8]. They have high durability from poisonous reagents, high thermal stability, wide thermal operation range, high regeneration capability and excellent NO<sub>x</sub> conversion efficiency. However, after a series of regeneration cycles they become deactivated and obsolete. Deactivated or spent SCR catalyst pose a great environmental risk, not only due to the necessity of having landfill spaces but also due to the toxicity of vanadium oxide when leached into the ground and water [9-11].

The investigation carried out by our research group [11-14] includes a selective leaching of titanium while tungsten and vanadium are keeps soluble in the leaching solution. The process is carried out through soda roasting followed by water leaching leading to generate the leach solution bearing around ~8000 mg/L

**\*Corresponding Author :**

E-mail: rkumarphd@kigam.re.kr

tungsten and ~1200 mg/L vanadium [11-14]. Hence, the real issue for this leach solution is to extract and separate vanadium and tungsten from the above leached solution.

Therefore, this work aims to develop a promising liquid-liquid extraction technology with usage of several commercial extractants for effective enrichment and separation of tungsten and vanadium from the industrially processed leach liquor obtained from spent SCR catalyst. In this investigation, a variety of extractants and synergistic mixtures were compared in pro to discern the optimum agent to greatly enrich the spent SCR catalyst solution or to separate the title metals vanadium and tungsten.

## 2. EXPERIMENTAL

To determine the concentration of different metals in the solution ICP-OES (iCAP 6000 Series, Thermo Scientific, USA) was used. To prepare the leach liquor used in the investigation, the spent SCR catalyst was obtained from the Samcheampo Thermoelectric Company, Korea having the following composition shown in Table 1

*Table 1. Elemental composition of spent SCR catalyst*

Compound	TiO <sub>2</sub>	SiO <sub>2</sub>	WO <sub>3</sub>	CaO	Al <sub>2</sub> O <sub>3</sub>	V <sub>2</sub> O <sub>5</sub>	Fe <sub>2</sub> O <sub>3</sub>	MoO <sub>3</sub>
wt. %	70.9	9.8	7.1	2.5	2.4	0.98	0.25	0.12

The leach liquor used for liquid-liquid extraction experiments was produced by alkali fusion of the spent SCR catalyst followed by water leaching. For the alkali fusion process, sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) purchased from Kanto Chemicals, Japan was used in a ratio SCR catalyst/ Na<sub>2</sub>CO<sub>3</sub> 1:1.2, and roasted at a temperature of 1000°C. The subsequent water leaching was done at 80°C, with a solid/liquid ratio 0.2 for 1 hour being stirred at 350 rpm. The solid residue was filtered using vacuum filtration and the leach liquor was used for further solvent extraction experiments.

The different commercial extractants were used as received from the manufacturer and as diluent Exxsol D80™ was used. The initial pH of the solution was measured as 14 and to reduce pH different acids HCl and H<sub>2</sub>SO<sub>4</sub> were used of analytical grade.

The liquid-liquid extraction was performed taking the same aliquot of aqueous and organic phase and contacting them in separating funnels during the determined time. The solvent extraction process was done in an incubated shaker at 250 rpm. For the process various calculations were performed to determine the process overall effectiveness and the separation capabilities of the different extractants

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

Where, M represents vanadium or tungsten.

$$\% \text{ Extraction} = \frac{D \cdot 100}{D + 1 \text{ (unit phase ratio)}} \quad (2)$$

### 3. RESULTS AND DISCUSSION

#### 3.1. Feed analysis

The initial pH of the spent SCR catalyst leach liquor was measured at 14 and two mineral acids, H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub> concentrated were used to modify the pH to understand the influence of pH on the extraction by different extractants. When the pH of the leach liquor was adjusted to 10 and 7.6 there was precipitation in the leach liquor, which was further analyzed by SEM as shown in Figure 1. In addition, due to the precipitation of the metals the concentration of the metals is greatly reduced at pH 10 when adjustment was done with HCl and at pH 7.6 when adjustment was done with H<sub>2</sub>SO<sub>4</sub> as shown in Table 2.

Table 2. concentration of vanadium and tungsten in the feed solution at different pH

pH condition	Vanadium, mg/L	Tungsten, mg/L
14.00	1238	8635
<b>Adjusted with HCl</b>		
10.00	645	4556
7.60	1021	7249
<b>Adjusted with H<sub>2</sub>SO<sub>4</sub></b>		
10.00	1152	8004
7.60	705	5547

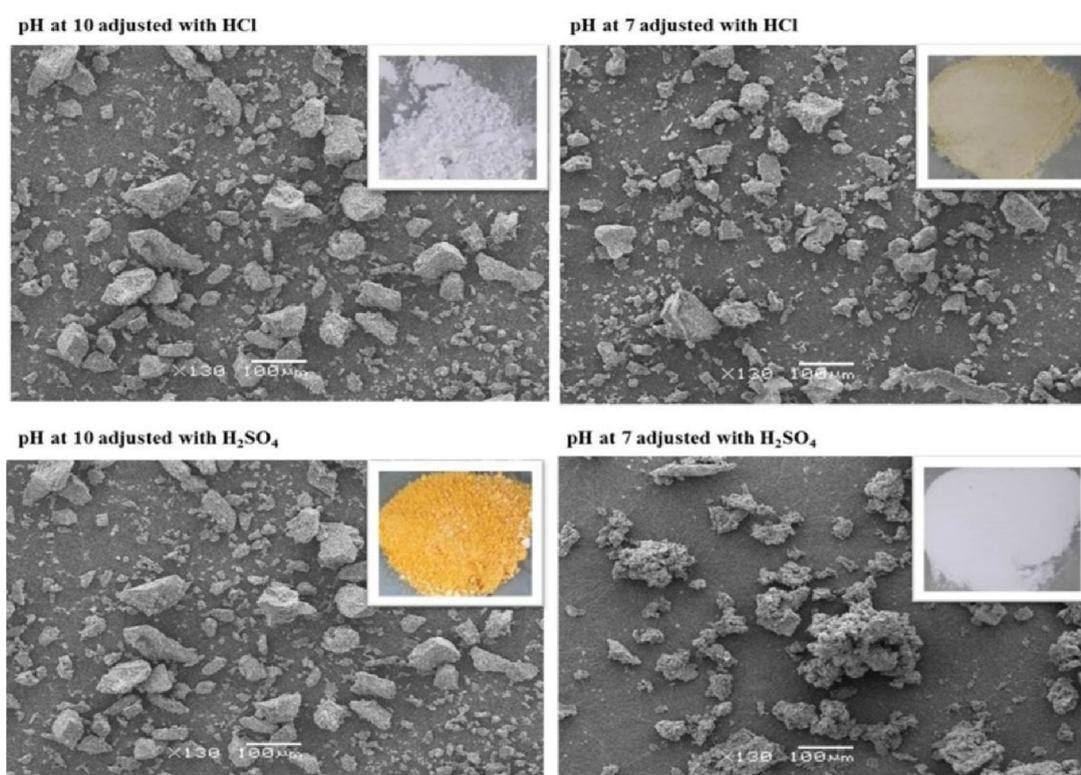


Figure 1. Solids precipitated at different pH from the spent SCR catalyst leach liquor

On the other hand, both tungsten and vanadium are commonly known for exhibiting variable oxidation states when acidity conditions are modified. Depending on this parameter, either of these metals are found to exist as cation and /or anion moieties. In alkaline media vanadium is mostly present as anionic species such as  $\text{HVO}_4^{2-}$ ,  $\text{V}_4\text{O}_{12}^{4-}$ ,  $\text{H}_2\text{VO}_4^-$ ,  $\text{V}_3\text{O}_9^{3-}$ ,  $\text{V}_2\text{O}_7^{4-}$  and  $\text{VO}_4^{3-}$  while at slightly acidic media  $\text{pH} > 4$ ,  $\text{V}_4\text{O}_9^{2-}$  and  $\text{HV}_{10}\text{O}_{28}^{5-}$  are found as the predominant species. In the case of tungsten, the aqueous chemistry tends to be more complicated due to the slow reactions and paratungstates formation. While at  $\text{pH} < 6$  several oxo-anionic species are formed [15,16] such as  $\text{HWO}_4^-$ ,  $\text{H}_3\text{W}_6\text{O}_{21}^{3-}$ ,  $\text{HW}_6\text{O}_{21}^{5-}$ ,  $\text{H}_2\text{WO}_4$  and  $\text{W}_6\text{O}_{21}^{6-}$ .

Due to the variability of the species and the complex aqueous chemistry of vanadium and tungsten it was observed that pH and concentration of the metals varied with time in the feed solution as shown in Table 3.

**Table 3. variation of the initial pH and concentration of vanadium and tungsten in the feed solution with time**

Time	pH	Vanadium, mg/L	Tungsten, mg/L
1 min	6.8	596	7049
10 min	6.8	562	7169
30 min	6.8	570	7400
1 hour	8.0	588	7613
2 hours	8.3	597	7609
3 hours	8.3	600	7709
6 hours	8.4	646	8335
10 hours	8.4	682	8732
24 hours	8.6	656	8413
30 hours	8.7	660	8541
48 hours	8.7	741	9376

### 3.2. Effect of the pH on the extraction for different amine and phosphorous-based extractants

For solvent extraction, the experimental parameters were kept constant: temperature 25°C, A/O ratio 1 and extraction equilibrium time was 5 min. As observed in Figure 2 decreasing the pH for different amine-based extractants leads to an increase in the extraction efficiency of the tertiary amines (Alamine 336, 304, 304-I & 308) while in the case of the quaternary ammonium salt (Aliquat 336) the maximum extraction efficiency was reached at initial pH 4 (Eq pH 6.1) and then it reached a plateau. Whilst all the tertiary amines show and almost complete extraction of both metals when the initial pH is 2.0 (Eq. pH 2.3) except in the case of Alamine 304, which maximum extraction efficiency is 21% for tungsten and 14% for vanadium. The results obtained for the quaternary ammonium salt and for the tertiary amines when pH is modified are in agreement with the mechanism of extraction shown in literature when these extractants have been used to recover a variety of metals [17-22].

In the case of phosphorous-based extractants, it can be observed from Figure 3 that varying the pH from initial pH 6 to 2 does not have a great effect in the extraction efficiency of vanadium and tungsten, which is minimum

for D2EHPA, PC88A and Cyanex 272. As observed, the maximum extraction is for vanadium at an initial pH of 3 using D2EHPA as the extractant. However, in all the other cases for all the studied pH the extraction of both title metals were lower than 25%, which is not quantitative.

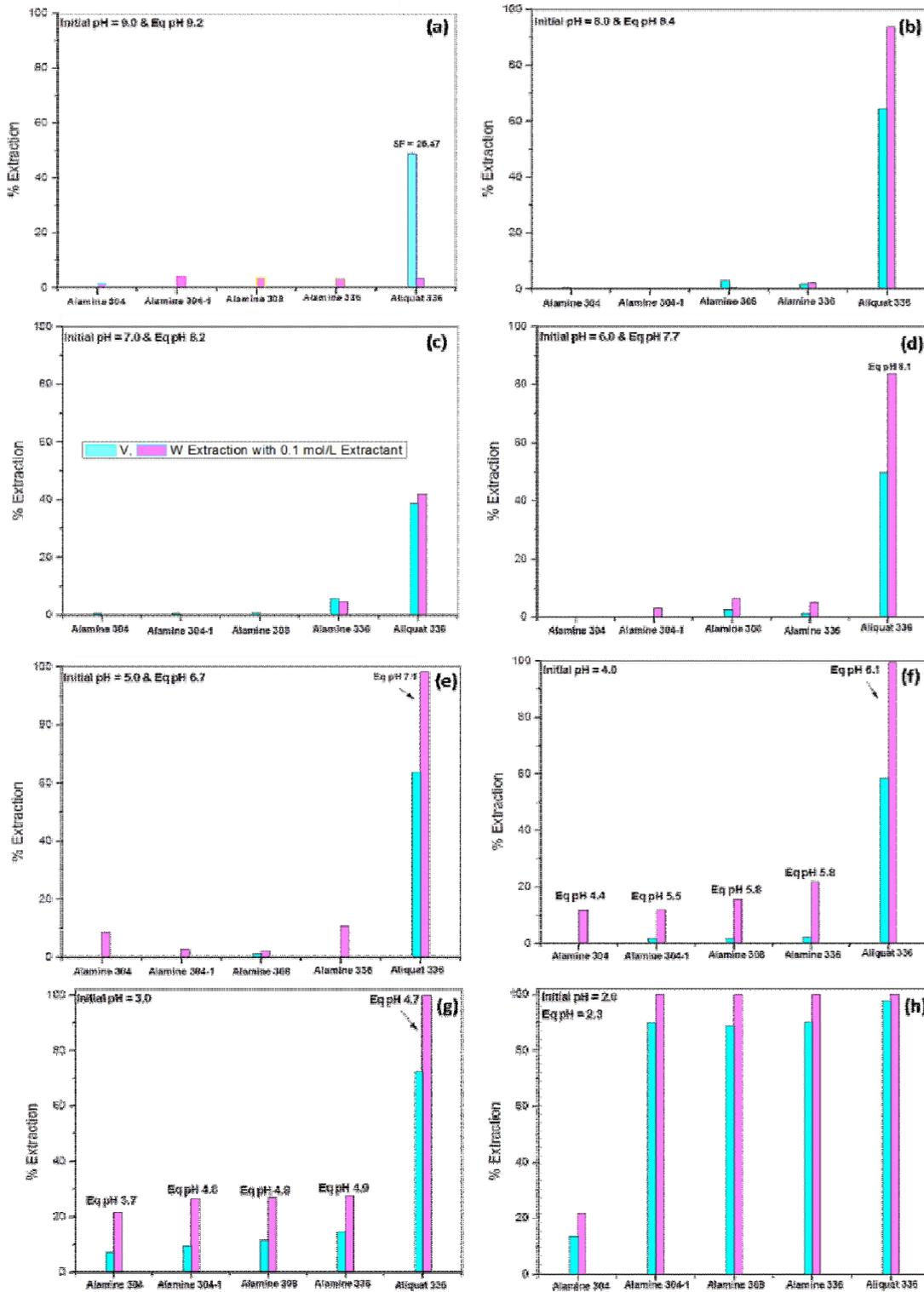


Figure 2. Extraction efficiency for different amine based extractants with a concentration of 0.1 mol/L at initial pH (a) 9.0 (b) 8.0 (c) 7.0 (d) 6.0 (e) 5.0 (f) 4.0 (g) 3.0 & (h) 2.0

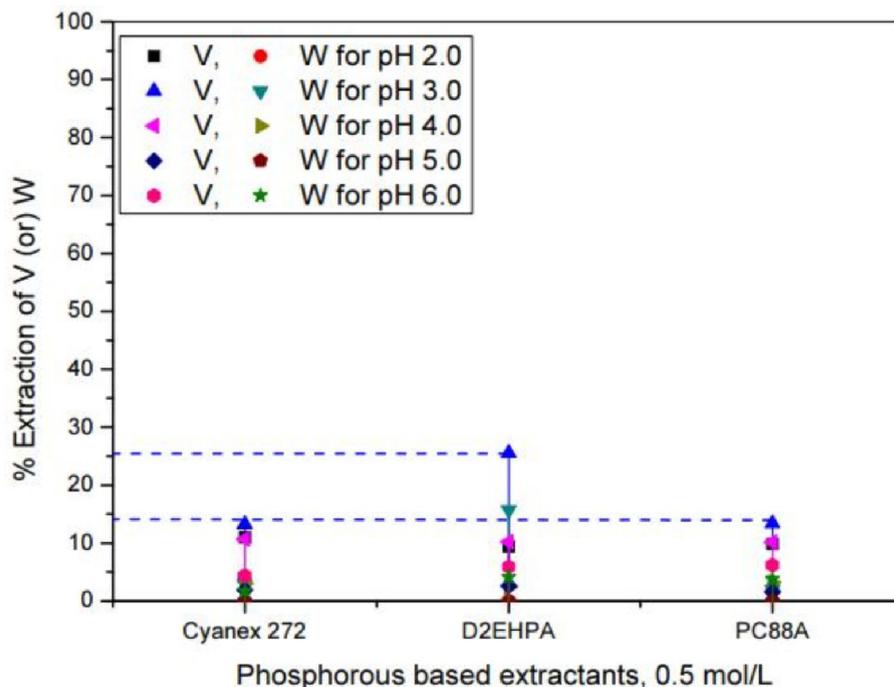


Figure 3. Extraction efficiency for different phosphorous-based extractants with a concentration of 0.5 mol/L

### 3.3. Comparison of various mixtures of extractants

Based on above study, the pH of the leach liquor was adjusted to 10, partially the leach liquor get precipitated then the solid and liquid was separated by vacuum filtration. The remaining leach liquor was used for W and V recovery studies. The solvent extraction of the title metals by a mix of various extractants was carried out with fixed experimental conditions (temperature 25°C, A/O ratio 1 and extraction equilibrium time was 5 min). The obtained data was presented in Figure 4 (a). Three combinations of the extractant systems such as Aliquat 336 with TBP (or) D2EHPA (or) Cyanex 272 extracted the both metals such as W and V 99.9%. It can be concluded that Aliquat 336 shows great potential for extraction of both metals; however, it is necessary to further study selective recovery of each metal from loaded organic phase. The individual extractant system 0.2 mol/L Aliquat 336 shown very good separation factor (SF) for V and W ( $SF = DV/DW$ , Where D = Distribution ratio of the metal from aqueous phase to organic phase) SF is 137.5.

Additionally, the SCR spent catalyst leach liquor initial pH was adjusted from 14 to 7.6, showing precipitation at these conditions. The precipitate was filtered by vacuum filtration then the remaining pregnant liquor was further processed for W and V extraction and possible separation. The experimental parameters were kept constant: temperature 25°C, A/O ratio 1 and extraction equilibrium time was 5 min. The obtained experimental results were presented in Figure 4 (b). Resulting data shows that for all combinations of extractant vanadium and tungsten are extracted simultaneously showing a very vague possibility of separation.

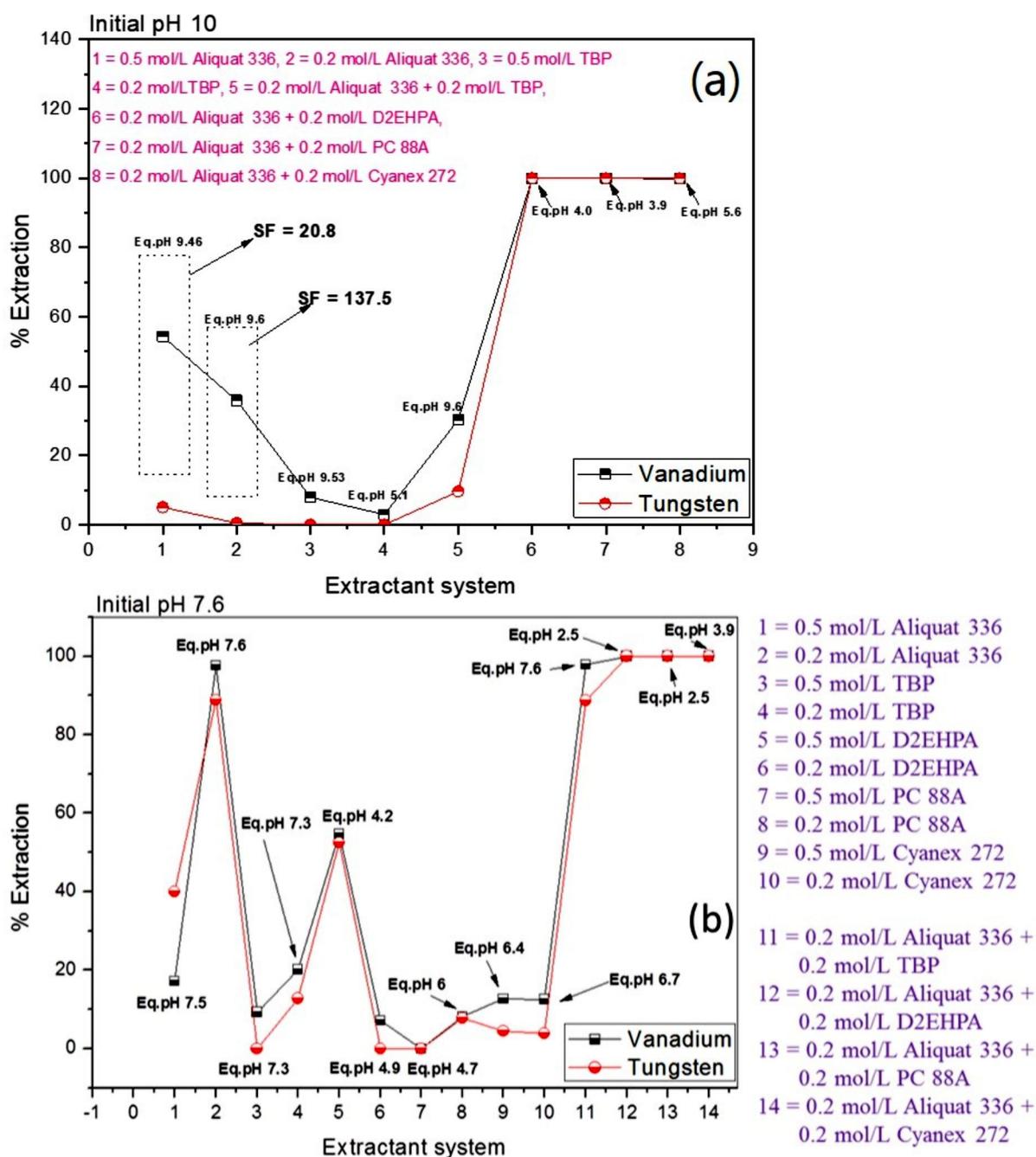


Figure 4. Extraction efficiency of mixed extractant systems at initial pH (a)10 & (b)7.6

### 3.4. Extraction isotherm (McCabe Thiele plots)

To construct the extraction isotherm, the spent SCR catalyst liquor holding 1712 mg/L of vanadium and 4097 mg/L of tungsten was contacted with different concentrations of Aliquat 336 at several phase ratio A:O while the total volume solution was constant. The initial pH of the solution was kept at 5.01 and extraction was done in 30 minutes. The Mc-Cabe Thiele plots for the extraction of W & V are presented in Figure 5. The results

show that at A: O = 5 there is a quantitative extraction of vanadium in three stages, while at A: O = 8 tungsten can be enriched 8 times in a two-stage counter current extraction process. Thus, due to the high concentration of tungsten in relation to vanadium A: O = 8 is chosen for enrichment while one extra stage is added to ensure that the extraction process yield is achieved.

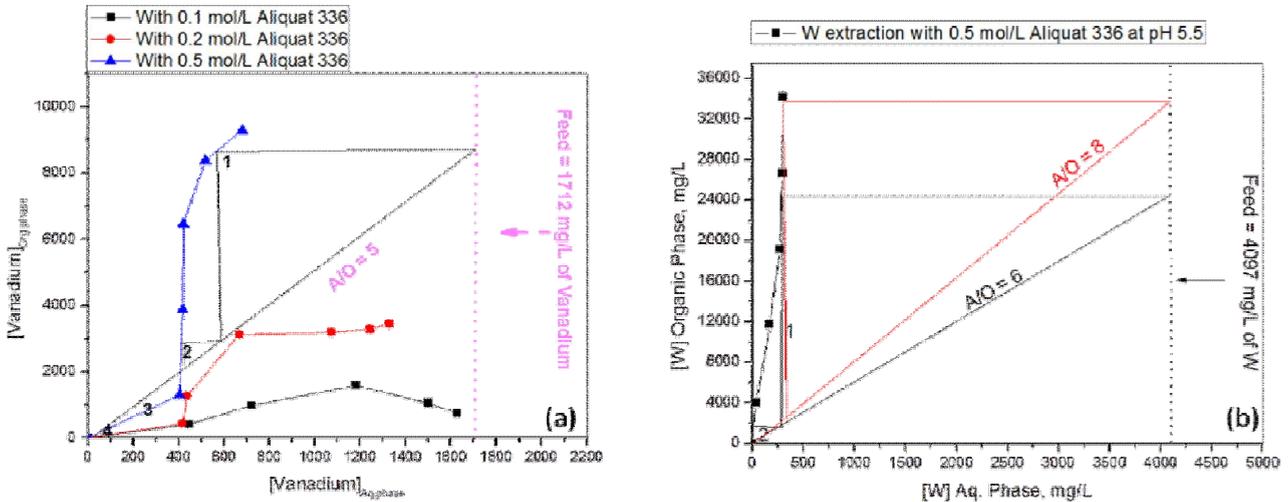


Figure 5. Extraction isotherm for (a) Vanadium & (b) Tungsten

### 3.5. Stripping studies

For the stripping studies, the loaded organic (LO) obtained using the results from the extraction isotherm containing approximately 9 g/L of Vanadium and 33 g/L Tungsten were used to determine the stripping conditions for the recovery of metals. Based on several studies by different researchers it was noted that sodium hydroxide could be a potential effective stripping agent for the loaded organic [23-25]. Thus, stripping was carried out in A:O = 1, temperature = 298K and at different concentrations of NaOH to investigate the effectivity in stripping. As shown in Figure 6 when increasing the NaOH concentration to 1 mol/L there is a stripping up to 99% of tungsten and 90% of vanadium.

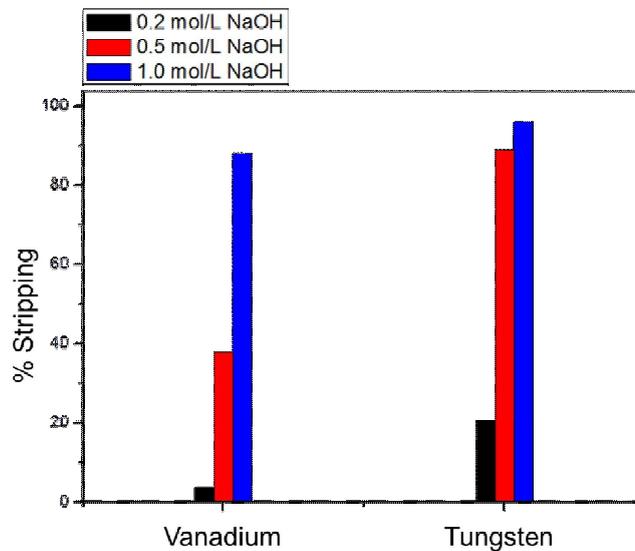


Figure 6. Stripping efficiency of vanadium and tungsten from loaded organic

#### **4. CONCLUSIONS**

In the present study, several commercial extractants (amine-based and phosphorous-based) were explored for the selective extraction or enrichment of vanadium and tungsten from spent SCR catalyst. In the case of the phosphorous-based extractants the highest extraction efficiency obtained was around 25% for vanadium at initial pH 3 with D2EHPA, thus phosphorous-based extractants are considered not suitable for the recovery of vanadium and tungsten from spent SCR catalyst. On the other hand, several amine-based extractants were considered for the same purpose and it was concluded that the best commercial extraction agent for vanadium and tungsten simultaneous extraction and enrichment is Aliquat 336 followed by Alamine 304, Alamine 336, Alamine 304-I and Alamine 308. Aliquat 336 extracts both metals almost to a 99.9% effectivity at initial pH of 4 while in the case of the tertiary amines due to the protonation necessity of the amine to be reactive with anions, lower pH are necessary (initial pH 2 or 3). After establishing the best extractant, an extraction isotherm was derived and it was determined that there could be 8 fold enrichment of vanadium and tungsten in three counter-current stages, followed by an almost complete stripping of the loaded organic using NaOH 1 mol/L.

#### **ACKNOWLEDGMENT**

This research was supported by the Basic Research Project (22-3803) of the Korea Institute of Geoscience and Mineral Resources (KIGAM) funded by the Ministry of Science and ICT of Korea.

#### **REFERENCES**

- [1] S.H. Su, S.Y. Feng, Y.F. Zhao, Q. Lu, W.L. Cheng, C.Q. Dong, Comparison of Three Types of NH<sub>3</sub>-SCR Catalysts, *Appl. Mech. Mater.* 130-134 (2011) 418-421. <https://doi.org/10.4028/www.scientific.net/AMM.130-134.418>.
- [2] M. Renzi, F. Cerza, C. Gariazzo, N. Agabiti, S. Cascini, R. Di Domenicantonio, M. Davoli, F. Forastiere, G. Cesaroni, Air pollution and occurrence of type 2 diabetes in a large cohort study, *Environ. Int.* 112 (2018) 68-76. <https://doi.org/10.1016/j.envint.2017.12.007>.
- [3] M.E. Munawer, Human health and environmental impacts of coal combustion and post-combustion wastes, *J. Sustain. Min.* 17 (2018) 87-96. <https://doi.org/10.1016/j.jsm.2017.12.007>.
- [4] F. Nakajima, I. Hamada, The state-of-the-art technology of NO<sub>x</sub> control, *Catal. Today.* 29 (1996) 109-115. [https://doi.org/10.1016/0920-5861\(95\)00288-X](https://doi.org/10.1016/0920-5861(95)00288-X).
- [5] M. Radojevic, Reduction of nitrogen oxides in flue gases, *Environ. Pollut.* 102 (1998) 685-689. [https://doi.org/https://doi.org/10.1016/S0269-7491\(98\)80099-7](https://doi.org/https://doi.org/10.1016/S0269-7491(98)80099-7).
- [6] E. Asadi Dalini, G. Karimi, S. Zandevakili, M. Goodarzi, A Review on Environmental, Economic and Hydrometallurgical Processes of Recycling Spent Lithium-ion Batteries, *Miner. Process. Extr. Metall. Rev.* (2020) 1-22. <https://doi.org/10.1080/08827508.2020.1781628>.
- [7] J.L. Sorrels, D.D. Randall, K.S. Schaffner, C.R. Fry, Chapter 2 Selective Catalytic Reduction, *Econ. Cost Anal. Air Pollut. Regul.* (2016). <https://doi.org/10.1016/j.fertnstert.2015.01.016>.

- [8] F. Ferella, A review on management and recycling of spent selective catalytic reduction catalysts, *J. Clean. Prod.* 246 (2020) 118990. <https://doi.org/10.1016/j.jclepro.2019.118990>.
- [9] M. Imtiaz, M.S. Rizwan, S. Xiong, H. Li, M. Ashraf, S.M. Shahzad, M. Shahzad, M. Rizwan, S. Tu, Vanadium, recent advancements and research prospects: A review, *Environ. Int.* 80 (2015) 79-88. <https://doi.org/10.1016/j.envint.2015.03.018>.
- [10] J.H. Jeon, A.B. Cueva Sola, J.-Y. Lee, R.K. Jyothi, Hydrometallurgical process development to recycle valuable metals from spent SCR deNOX catalyst, *Sci. Rep.* 11 (2021) 22131. <https://doi.org/10.1038/s41598-021-01726-0>.
- [11] R.K. Jyothi, G. Moon, H.-R. Kim, J.-Y. Lee, I.H. Choi, Spent V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> catalyst processing for valuable metals by soda roasting-water leaching, *Hydrometallurgy*. 175 (2017) 292-299. <https://doi.org/10.1016/j.hydromet.2017.12.010>.
- [12] I.H. Choi, G. Moon, J.Y. Lee, R.K. Jyothi, Extraction of tungsten and vanadium from spent selective catalytic reduction catalyst for stationary application by pressure leaching process, *J. Clean. Prod.* 197 (2018) 163-169. <https://doi.org/10.1016/j.jclepro.2018.06.196>.
- [13] H.I. Kim, G. Moon, I.H. Choi, J.Y. Lee, R.K. Jyothi, Hydrometallurgical process development for the extraction, separation and recovery of vanadium from spent desulfurization catalyst bio-leach liquors, *J. Clean. Prod.* 187 (2018) 449-458. <https://doi.org/10.1016/j.jclepro.2018.03.247>.
- [14] I.H. Choi, G. Moon, J.Y. Lee, R.K. Jyothi, Hydrometallurgical processing of spent selective catalytic reduction (SCR) catalyst for recovery of tungsten, *Hydrometallurgy*. 178 (2018) 137-145. <https://doi.org/10.1016/j.hydromet.2018.04.011>.
- [15] T.H. Nguyen, M.S. Lee, A review on the separation of molybdenum, tungsten, and vanadium from leach liquors of diverse resources by solvent extraction, *Geosystem Eng.* 19 (2016) 247-259. <https://doi.org/10.1080/12269328.2016.1186577>.
- [16] T. Nakamura, S. Nishihama, K. Yoshizuka, A novel extractant based on d-glucosamine for the extraction of molybdenum and tungsten, *Solvent Extr. Res. Dev.* 16 (2009) 47-56.
- [17] A.B. Cueva-Sola, P.K. Parhi, J.-Y. Lee, R.K. Jyothi, Sustainable environmentally friendly approaches to the recycling of spent selective catalytic reduction (SCR) catalysts, in: *Sustain. Nanotechnol. Environ. Remediat.*, Elsevier, 2022: pp. 765-787. <https://doi.org/10.1016/B978-0-12-824547-7.00008-4>.
- [18] J.Y. Lee, B. Raju, B.N. Kumar, J.R. Kumar, H.K. Park, B.R. Reddy, Solvent extraction separation and recovery of palladium and platinum from chloride leach liquors of spent automobile catalyst, *Sep. Purif. Technol.* 73 (2010) 213-218. <https://doi.org/10.1016/j.seppur.2010.04.003>.

- [19] C.J. Kim, J.R. Kumar, J.S. Kim, J. Y. Lee, H.S. Yoon, Solvent extraction studies on uranium using amine based extractants and recovery from low grade ore leach liquors, *J. Braz. Chem. Soc.* 23 (2012) 1254-1264. <https://doi.org/10.1590/S0103-50532012000700009>.
- [20] K. Larsson, K. Binnemans, Selective extraction of metals using ionic liquids for nickel metal hydride battery recycling, *Green Chem.* 16 (2014) 4595-4603. <https://doi.org/10.1039/c3gc41930d>.
- [21] V.N.H. Nguyen, M.N. Le, M.S. Lee, comparison of extraction ability between a mixture of almine 936/ Aliquat 336 and D2EHPA and ionic liquid A Li-D2 from weak hydrochloric acid solution, *Metals.* 10-12 (2020) 1678
- [22] B.D. Pandey, V. Kumar, D. Bagchi, R.K. Jana, Premchand, Processing of tungsten preconcentrate from low grade ore to recover metallic values, *Miner. Process. Extr. Metall. Rev.* 22 (2001) 101-120. <https://doi.org/10.1080/08827509808962491>.
- [23] Y.A. El-Nadi, N.S. Awwad, A.A. Nayl, A comparative study of vanadium extraction by Aliquat-336 from acidic and alkaline media with application to spent catalyst, *Int. J. Miner. Process.* 92 (2009) 115-120. <https://doi.org/10.1016/j.minpro.2009.03.005>.
- [24] Y. Bal, K.E. Bal, G. Cote, A. Lallam, Characterization of the solid third phases that precipitate from the organic solutions of Aliquat® 336 after extraction of molybdenum(VI) and vanadium(V), *Hydrometallurgy.* 75 (2004) 123-134. <https://doi.org/10.1016/j.hydromet.2004.07.004>.
- [25] R.K. Mishra, P.C. Rout, K. Sarangi, K.C. Nathsarma, Solvent extraction of Fe(III) from the chloride leach liquor of low grade iron ore tailings using Aliquat 336, *Hydrometallurgy.* 108 (2011) 93-99. <https://doi.org/10.1016/j.hydromet.2011.03.003>.