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Tungsten Recovery from Spent SCR Catalyst Using Alkaline Leaching and Ion Exchange

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Abstract: The recovery of tungsten (W) from a honeycomb-type spent selective catalytic reduction (SCR) catalyst using an alkaline leaching–ion exchange method was investigated. Spent SCR catalyst mainly consists of TiO_2 and other oxides (6.37% W, 1.57% vanadium (V), and 2.81% silicon (Si), etc.). The ground catalyst was leached at the optimal conditions, as follows: NaOH concentration of 0.3 kg/kg of catalyst, pulp density of 3%, leaching temperature of 70 °C, particle size of −74 μm, and leaching time of 30 min. In this study, the leaching rate values of V and W under the above conditions were 87 wt %, and 91 wt %, respectively. The pregnant solution was then passed through a strong base anion exchange resin (Amberlite IRA900). At high pH conditions, the use of strong base anion exchange resin led to selective loading of divalent WO_4^{2-} from the solution, because the fraction of two adjacent positively-charged sites on the IRA900 resin was higher and separate from the coexisting VO_4^{3-}. The adsorbed W could then be eluted with 1 M NaCl + 0.5 M NaOH. The final concentrated W solution had 8.4 g/L of W with 98% purity. The application of this process in industry is expected to have an important impact on the recovery of W from secondary sources of these metals.

Keywords: tungsten recovery; spent SCR catalyst; leaching-ion exchange

1. Introduction

Nitrogen oxides (NO_x, x = 1, 2) contribute to a series of environmental issues. Selective catalytic reduction (SCR) with ammonia is one of the most successful methods for the elimination of nitrogen oxide emissions from stationary sources and diesel vehicles [1,2]. The honeycomb monolith V_2O_5–WO_3/TiO_2 catalyst with V_2O_5 as the primary active phase and WO_3 as the activity promoter is the representative catalyst used in the NH_3–SCR system [3,4]. After several cycles of regeneration of deactivated catalyst, the catalyst becomes waste, which can be either stored or processed to recover valuable metals. However, storage of spent catalyst is environmentally unacceptable, as it contains leachable hazardous metals such as tungsten (W) and vanadium (V). There is emerging evidence that W has toxic health effects [5]. Additionally, V pollution is becoming a major environmental concern and has toxic effects on the growth of plants and animals [6]. In Taiwan, the amount of spent NH_3-SCR catalyst generated is currently 1000 tons·year^{-1} [7]. This will increase further in the coming years, because the environmental laws concerning NO_x emissions have become increasingly strict [8]. Spent NH_3-SCR catalyst generally contains titanium oxide and metals such as W and V in appreciable concentrations, and thus could be used as a secondary source for these valuable metals. In general, the recovery of valuable metals from spent catalysts has been carried out by conventional methods [9–13], such as acid leaching, caustic leaching, and salt roasting followed by leaching with water. Among these, caustic leaching seems to be the best option for the recovery of SCR catalyst, since WO_3 is insoluble in acid. Once in solution, the metals can be isolated in a pure form using established methods, such as selective precipitation [14,15], solvent extraction [16,17], and ion exchange [18,19]. V and W exhibit

very similar chemical properties and are produced commercially by relatively similar procedures [20]. Therefore, it is difficult to separate V from W. However, in alkaline solution, V and W exist as $VO_4{}^{3-}$ and $WO_4{}^{2-}$, respectively [21–23]; therefore, the difference in the number of negative charges may be exploited to separate V and W using ion exchange. However, very few reports are available on the recovery W and V from spent SCR catalyst [24]. In this paper, we report on the results of studies to develop a process based on single-step leaching of spent SCR catalyst with sodium hydroxide solution, followed by separation and recovery of W and V from the leach liquor using ion exchange.

2. Materials and Methods

2.1. Materials

The spent catalyst was obtained from a steel plant in the form of 3–4 mm particles. A 0.1 g ground sample was digested using aqua regia at 100 °C for 30 min. After cooling and filtration, the composition of the filtrate was determined using a flame atomic absorption spectrometer (FAAS, Perkin Elmer AAnalyst 100, PerkinElmer, Waltham, MA, USA). The main elemental composition is shown in Table 1, together with minor amounts of Ca, Al, and P. The specific surface area was determined to be 32 $m^2 \cdot g^{-1}$ by Brunauer–Emmett–Teller (BET) specific area analyzer (Micrometrics ASAP 2000, Micromeritics Corp., Norcross, GA, USA). A macroporous type 1 strong base anion exchange resin containing quaternary ammonium salt groups, Amberlite IRA900 (Rohm and Haas, Rohm and Haas Chemicals, Philadelphia, PA, USA), was used in the experiments. IRA900 resin, with 0.65–0.82 mm particle size, was in the chloride form and was used as received. All of the reagents used in the tests were of analytical grade.

Table 1. Elemental compositions of V-W/TiO$_2$ type spent catalyst.

Component	Ti	Si	W	V
wt %	33.40	2.81	6.37	1.57

2.2. Leaching Experiments

Leaching experiments were conducted in a 250 mL flask fitted with a seal to avoid evaporation loss. The contents were stirred with a magnetic stirrer and heated in a water bath. The spent catalyst was ground and sieved using various mesh-size sieves. The required amounts of distilled water and NaOH were transferred to the reactor and placed in a water bath. Once the test temperature was reached, a calculated amount of catalyst sample was added to the reactor. The final solution was filtered to eliminate residual particles, and the filtrate was analyzed for W, V, and Si using a FAAS with an air–acetylene flame to estimate leaching efficiency. All analyses were run in duplicate, and the mean values were considered. The results were found to vary within 3%. The filtrate was collected and used in the ion-exchange experiments in this work. The studied parameters include NaOH dosage, pulp density, leaching temperature, particle size, and leaching time.

2.3. Column Experiments

The separation of tungsten from vanadium with the anion exchange resin was carried out in a glass column (10 cm long and 0.7 cm in diameter) which operated with the feed liquor at room temperature. The dry resin (3.5 mL) was wet-packed into the glass column. A fixed volume of feed liquor was passed through the column at a constant flow rate, and the effluent was collected as a whole to determine the contents of tungsten and vanadium. In other experiments, samples were collected periodically from the column effluent and analyzed to determine the breakthrough curves. The loaded resin from the column tests was eluted with a mixture of NaCl and NaOH using a downstream flow at a constant flow rate.

3. Results and Discussion

3.1. Leaching of V and W

3.1.1. Effects of NaOH Concentration

The effects of initial NaOH addition on the leaching of V and W were examined at 0.1 to 1.5 kg/kg of catalyst. The leaching process was carried out under the following conditions: particle size, −37 μm; pulp density ratio, 1.0% (*w/v*); reaction time, 60 min; reaction temperature, 70 °C; and stirring speed, 400 rpm. The results shown in Figure 1 indicate that the extraction of V and W increases as the NaOH addition increases in the leaching process. The amount of such metals in the leaching solution increases when NaOH addition varies from 0 to 0.5 kg/kg of catalyst. As the NaOH addition increases from 0.5 to 1.5 kg/kg of catalyst, the extraction of V and W remains almost constant. These results can be explained by the fact that increasing the NaOH concentration results in an increase in the OH^- ions available to react with the catalyst to form soluble complexes, such as WO_4^{2-} and VO_4^{3-}. From Figure 1, it can be observed that NaOH addition of 0.3 and 0.5 kg/kg of catalyst have almost same reaction efficiencies, and this is why NaOH addition of 0.3 kg/kg of catalyst was considered in the further experiments.
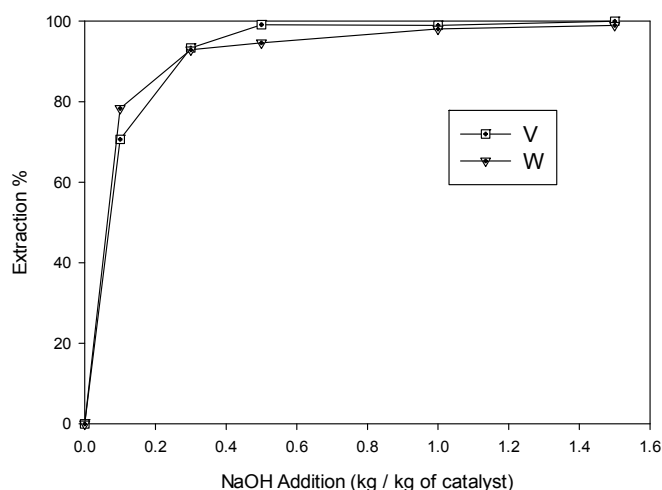

Figure 1. Effects of NaOH addition on the extraction efficiencies of W and V.

3.1.2. Effects of Pulp Density

The effects of solid loading on metal extraction was studied using 1%, 2%, 3%, 4%, and 6% (*w/v*) pulp densities. The leaching process was carried out under the following conditions: reaction temperature, 70 °C; NaOH addition, 0.3 kg/kg of catalyst; and stirring speed, 400 rpm. The experimental results shown in Figure 2 indicate that the extraction of V and W decreased with increasing pulp density. The increase in pulp density meant that the initial NaOH concentration in the liquor also increased, as the NaOH-to-catalyst ratio was the same in all experiments (0.3:1.0). Therefore, the rate limiting factor for extraction of V and W was probably mass transfer, and a high concentration of V and W in solution would decrease the mass-transfer rate, and so lower extraction efficiency. However, when the pulp density increases from to 1% to 3%, the extraction rate of V and W decreases slightly, but the leaching capacity significantly increases. The results thus show that the optimum pulp density is 3%.
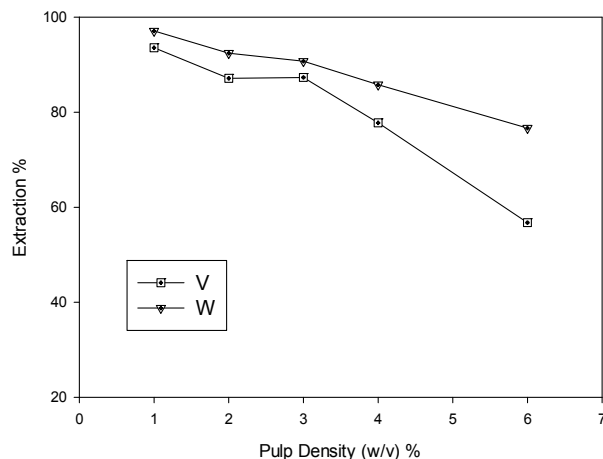
Figure 2. Effects of pulp density on the extraction efficiencies of W and V.

3.1.3. Effects of Temperature

The effects of temperature on the leaching of V and W were examined at 30 to 90 °C. The leaching process was carried out under the following conditions: pulp density, 3% (w/v); reaction time, 60 min; NaOH addition, 0.3 kg/kg of catalyst; and stirring speed, 400 rpm. The experimental results are shown in Figure 3. The results reveal that increasing the temperature can lead to a relatively significant improvement in the extraction efficiency of V. The extraction efficiency of V increases from 71.9% to 87.3% when the leaching temperature increases from 30 to 70 °C. However, the extraction of W is insensitive to variations in temperature, and a constant leaching efficiency of 90% was achieved for the studied reaction temperatures. Therefore, 70 °C is considered as the optimum leaching temperature.
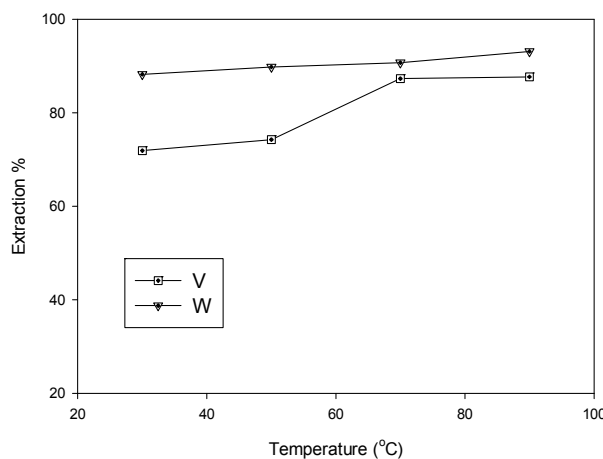

Figure 3. Effect of leaching temperature on the extraction efficiencies of W and V.

3.1.4. Effects of Particle Size

The effects of particle size on the leaching of V and W were examined using four different size fractions: 100% passing through −180, −74, and −37 μm. The leaching process was carried out under the following conditions: reaction temperature, 70 °C; pulp density, 3% (w/v); reaction time, 60 min; NaOH addition, 0.3 kg/kg of catalyst; and stirring speed, 400 rpm. The experimental results are shown in Figure 4. The results indicated that changes in particle size only slightly affect the extraction of V and W in the range studied, which means that under such leaching conditions, the maximum degree of mineral liberation has been reached. Therefore, −74 μm is considered as the optimum particle size for leaching.
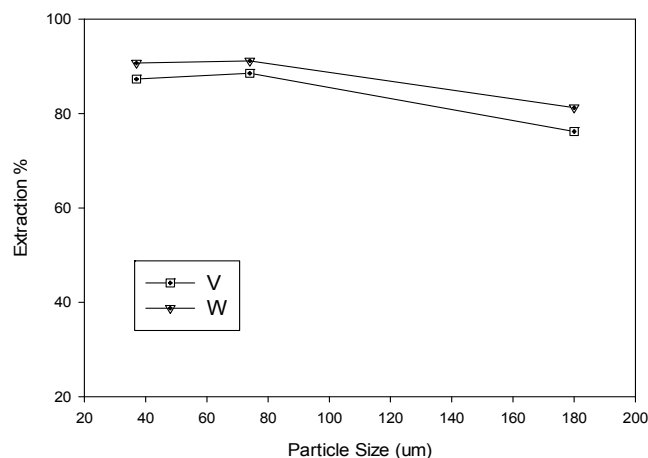
Figure 4. Effect of particle size on the extraction efficiencies of W and V.

3.1.5. Effects of Leaching Time

The effects of time from 25 to 90 min on the leaching of V and W were examined. The leaching process was carried out under the following conditions: pulp density, 3% (*w/v*); NaOH addition, 0.3 kg/kg of catalyst; and stirring speed, 400 rpm. The leaching of V and W reached 83.4 wt % and 85.9 wt %, respectively, in the first 30 min (Figure 5), demonstrating rapid leaching kinetics. Further increases in time do not improve the extraction, and thus 30 min is considered to be the optimum leaching time.
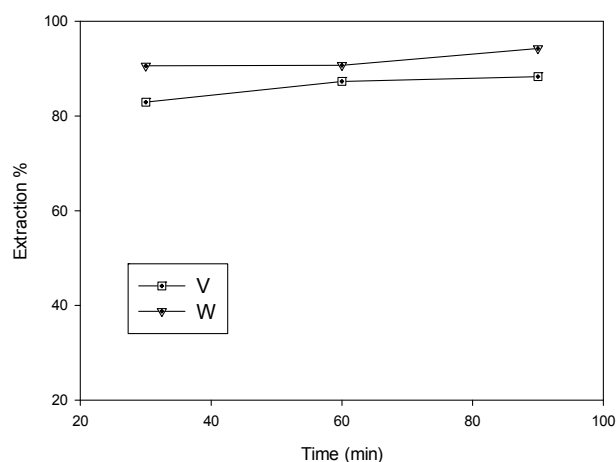

Figure 5. Effect of leaching time on the extraction efficiencies of W and V.

In summary, the optimal conditions for the leaching of spent SCR catalyst, as determined from the experiments of NaOH selective leaching, are as follows: NaOH concentration of 0.3 kg/kg of catalyst, pulp density of 3%, leaching temperature of 70 °C, particle size of −74 μm, and leaching time of 30 min. In this study, the leaching efficiencies of V and W under the above conditions were 87 wt %, and 91 wt %, respectively. The V and W were leached along with Si. This leachate consisted of (ppm) 409 V, 1679 W, and 851 Si at pH 13.5 was used in the ion exchange experiments.

3.2. Ion Exchange Separation of W

The initial experiments showed that when the pH value of the leachate (pH 13.5) was reduced to about 12.5, the Si in the leachate began to hydrolyze and precipitate, and considerable amounts of V and W were coprecipitated with Si. To minimize the loss of V and W, the pH of the leachate must

be maintained at pH > 12.5 for the ion exchange experiments. V and W exist as VO_4^{3-} and WO_4^{2-}, respectively, at pH > 12.5, and therefore a macroporous strong base anion exchange resin Amberlite IRA900 was used to separate V and W in this case.

3.2.1. Effects of the Effluent Volume

Table 2 presents a comparison of the effects of the column effluent volume on the separation of W, V, and Si by passing 14–86 bed volumes (BV) through the ion exchange columns. It can be seen that the strong base anion exchange resin (Amberlite IRA900) has a higher affinity for W than V and Si, and the separation efficiency depends on the passing volume. With the passing BV increasing from 14 to 43, the adsorption efficiency of W decreased from 99% to 59%, while the adsorption efficiency of V decreased from 11% to 4%. The adsorption capacity of resin for W and V is obviously exhausted after passing a certain BVs of solution. In addition, the purity of the adsorbed W (W/V ratio) increased along with the increasing passing BV, indicating that some of the V that was adsorbed early in the resin was replaced by W. It may thus be concluded that the separation of W from the leachate (pH 13.5) containing V and Si was possible due to ion exchange with Amberlite IRA900 resin.

Table 2. Effect of the effluent volume on the column separation of W, V, and Si. BV: bed volume.

Volume Passed Through Column (BV)	W Adsorbed (%)	V Adsorbed (%)	Si Adsorbed (%)	Adsorbed W/V Ratio
14	99.36	10.68	0.24	40
31	84.57	6.15	3.84	59
43	58.85	4.28	7.25	59
51	44.30	3.16	9.17	60
71	40.61	2.96	5.54	60
86	26.25	2.28	8.72	50

3.2.2. Effects of pH on Adsorption

The pH value of leachate solution is around 13.5. Therefore, leachate solutions with pH = 12.9, 13.5, and 13.8 were chosen to investigate the effects of pH on the separation of W and V. Table 3 shows the comparison of the effects of the solution pH on the V, W, and Si adsorption studied by passing 31 BV of leachate through the ion exchange columns. The results show that the pH value of the leachate had a significant influence on the separation of W and V. With the pH value increasing from 12.9 to 13.8, the adsorption efficiency of V decreased from 81% to 8%, while the adsorption efficiency of W remained around 95%. Obviously, the higher pH value was advantageous for the separation of W and V by IRA900 resin.

Table 3. Effect of pH on the column separation of W, V, and Si.

pH	W Adsorbed (%)	V Adsorbed (%)	Adsorbed W/V Ratio
12.9	98.01	81.39	4
13.5	97.64	13.78	28
13.8	93.80	8.24	52

It has been reported that V and W exist as VO_4^{3-} and WO_4^{2-}, respectively, at pH 13.5 [21–23]. According to ion exchange theory, higher valence VO_4^{3-} ions are more preferred by anion exchange resin over WO_4^{2-} ions. However, we found that anion exchange resin has a higher affinity for WO_4^{2-} than VO_4^{3-} at the high pH condition in this study.

In the high pH region, the concentration of positively-charged sites ($-N^+R_3$) on IRA900 resin decreases, due to the association of $-N^+R_3$ with OH^- ($-N^+R_3 + OH^- \rightarrow NR_3OH$). Reducing the number of positively-charged sites ($-N^+R_3$) on IRA900 resin, the probability of finding three adjacent positively-charged sites is low compared to that of finding two adjacent positively-charged sites on

IRA900 resin. In addition, according to ion exchange theory, three and two adjacent positively-charged sites are required to bind trivalent VO_4^{3-} and divalent WO_4^{2-} anions, respectively. Therefore, at the high pH condition, the use of anionic resin would lead to selective loading of divalent WO_4^{2-} from the solution, because the fraction of two adjacent positively-charged sites on IRA900 resin is higher. This proposed assumption perfectly explains the observed preferential adsorption of WO_4^{2-} anions on IRA900 resin at the high pH condition.

3.2.3. Column Tests

Loading Test

For the column loading experiment, the leachate solution was allowed to pass through the column packed with the IRA900 resin at a constant flow rate. The feed solution contained 409 mg/L V, 1679 mg/L W, and 851 mg/L Si at pH 13.5, and the flow rate was 1.7 BV/h. Figure 6 shows the normalized breakthrough curves for vanadium, tungsten, and silicon on IRA900 resin. It can be seen that both silicon and vanadium breakthrough immediately, while almost no tungsten presents in the effluent until the volume of liquid reaches 25 BV. The apparent sequence of affinity of metals on IRA900 resin is W > V = Si. This result is in line with the affinity of IRA900 toward W demonstrated in the effluent volume tests. The concentrations of V and Si in the effluent were slightly higher than those in the feed liquor, after bed volumes of 10, indicating that some of the V and Si that was adsorbed early in the resin was displaced from the resin by W with a stronger affinity for the resin. The loading stage was stopped when the sorption of W reached equilibrium, and became saturated when the ratio of C/C_0 approached 1.0 at approximately 25 BV. The loading of W on IRA900 resin at the saturation of W was found to be 50 g/L_{resin}. Amberlite IRA900 was found to be very selective for the extraction of W from alkaline leachate, and the separation of W from V and Si was highly efficient under the experimental conditions used in this work.
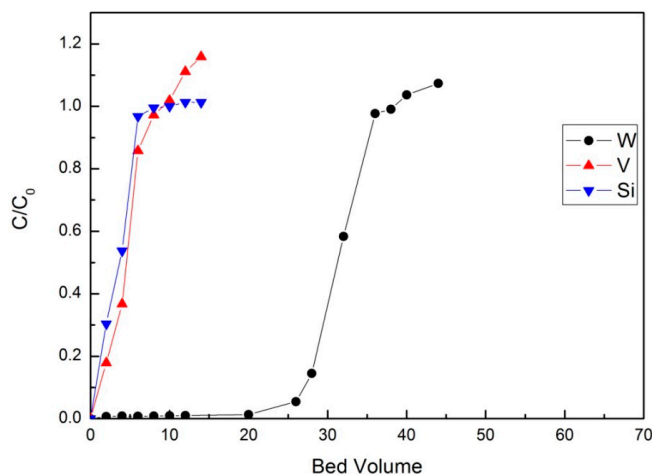

Figure 6. Normalized breakthrough curves (C/C_0 vs. BV) for V, W, and Si on IRA900 resin.

Stripping Test

The IRA900 resin is a strong base anion exchange resin with a quaternary ammonium salt group, which implies that the loaded resin can be desorbed by NaOH solution. After the loaded resin was washed by 1 BV de-ionized water, a 1 M NaCl + 0.5 M NaOH solution was used to strip W from the loaded resin, and the flow rate was 1.0 BV/h at ambient temperature. Figure 7 plots the elution curves for W elution from the loaded column. It can be seen that the loaded resin could be completely eluted using 1 M NaCl + 0.5 M NaOH solution. The stripping was completed when the eluate/resin volume ratio reached six, while the maximum concentration of W in the eluted solution could reach 22 g/L,

and the purity of the collected W is 98%. It can thus be concluded that IRA900 is an excellent resin to be utilized in extracting W from alkaline leachate.
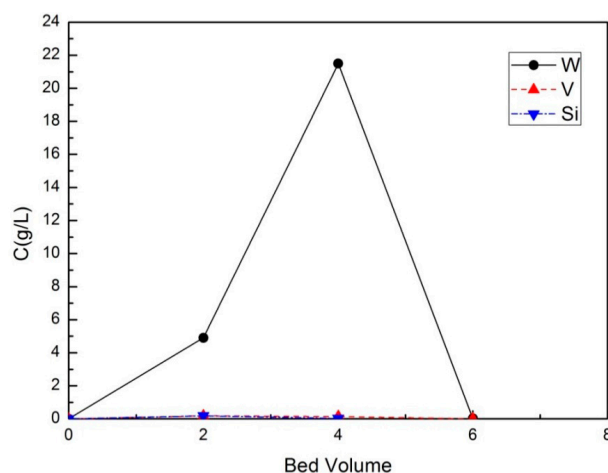

Figure 7. The elution curves for W elution from the loaded column.

3.3. Recycling Process of W from Spent SCR Catalyst

According to the experimental results, the recommended process for leaching W from spent SCR catalyst and its selective recovery from the leached solution using IRA900 resin is summarized in Figure 8. A solution with NaOH concentration of 0.3 kg/kg of catalyst is mixed with the ground sample (−74 μm) at a pulp density of 3%, and then leached at 70 °C for 30 min. The pregnant solution is then passed through the IRA900 resin. The loaded column is eluted with 1 M NaCl + 0.5 M NaOH, and concentrated W solution is collected. The effluent from the column may be further processed to recover V by chemical precipitation.
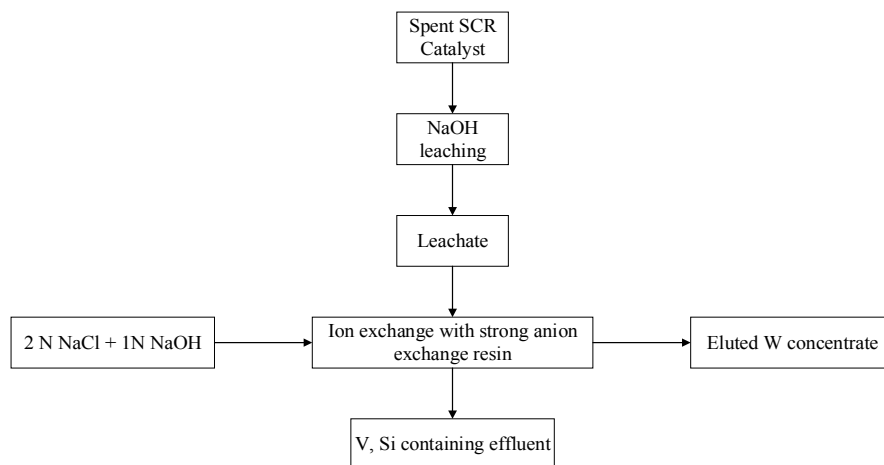

Figure 8. Proposed flow chart for the recovery of W from spent selective catalytic reduction (SCR) catalyst.

4. Conclusions

Studies were performed to develop a process using a leaching–ion exchange method to recover W from the spent SCR catalyst. According to the results of this work, the following conclusions were made: The optimal leaching conditions are: NaOH concentration of 0.3 kg/kg of catalyst, pulp density of 3%, leaching temperature of 70 °C, particle size of −74 μm, and leaching time of 30 min, which gave dissolution percentages for V and W of 87% and 91%, respectively. At the high pH condition, the use of strong base anion exchange resin lead to selective loading of divalent WO_4^{2-} from the solution,

because the fraction of two adjacent positively-charged sites on IRA900 resin is higher and separate from the coexisting $VO_4{}^{3-}$. The adsorbed W could then be eluted with 1 M NaCl + 0.5 M NaOH. The final concentrated W solution had 8.4 g/L of W with 98% purity. The application of this process in industry is expected to have a significant impact on the recovery of W from secondary sources of these metals.

Author Contributions: Wen-Cheng Wu performed the experiments, and analyzed and interpreted the data. Tang-Yi Tsai contributed to interpretation of the data. Yun-Hwei Shen was the Principal Investigator of this work and edited the paper.

Conflicts of Interest: The authors declare no conflict of interest.

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