Solvent extraction and separation of nickel and vanadium from sulfate leach liquor of power plant fly ash using D2EHPA and Cyanex 272

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Abstract

In this investigation, recovery and separation of nickel and vanadium from leach liquors of power plant fly ash were investigated by solvent extraction using D2EHPA, Cyanex 272, and their mixtures in various proportions. The mentioned fly ash mainly contains porous unburned carbon, sulfates, oxides of vanadium, nickel and iron. For this reason, synthetic sulfate solutions of nickel and vanadium were prepared in 2 gr/L of each metal. After dilution of the organic solvents in kerosene with the ratio of 1 to 4, experiments were carried out in the pH range of 1.0–7.0 in steps of 0.5 at ambient temperature. The investigation of solvent extraction of nickel and vanadium by sole D2EHPA was performed and the extraction percentages determined to be 90\% and 80\% for nickel and vanadium, respectively. However, the co-extraction of nickel and vanadium by D2EHPA can be increased with increasing equilibrium pH and temperature. It was shown that using sole D2EHPA, pH\textsubscript{50} (the pH at 50\% metal extraction) values for nickel and vanadium were 3.5 and 2, respectively; which is not appropriate for the efficient separation of nickel and vanadium simultaneously. Adding Cyanex 272 to D2EHPA in the organic phase, leads to a right shifting of extraction isotherm of nickel and a slight left shifting of the extraction isotherm of vanadium and finally improves the separation of nickel over vanadium. To optimize the recovery and separation process of nickel and vanadium from the sulfate leach liquor, the influence of different D2EHPA to Cyanex 272 ratios, various temperatures such as 25, 35, 45, and 55°C were studied. As a result, optimum separation of vanadium over nickel was achieved with a Cyanex 272 to D2EHPA ratio of 0.35 M: 0.25 M. Based on the optimum results, pH\textsubscript{50} values for nickel and vanadium were changed from 3.5 to 4.75 and from 2 to 1.75, respectively.

Keywords: Nickel, Vanadium, Solvent extraction, D2EHPA, Cyanex 272.

Introduction

Due to the wide applications of vanadium and nickel in the steel industry as alloying elements, ceaseless extraction of mineral resources of these two metals are becoming more and more insufficient to answer the rapid growing demands especially in industrialized countries. In recent years, mainly because of depleting in main sources of nickel and vanadium, researchers have been trying to discover and extract these metals from secondary sources such as fly ashes, crude oil, power plant residues, and spent catalysts [1, 2].
Fly ash generated by power plants is categorized as a special waste by US EPA. These residues from fossil fuel combustion are captured by pollution control equipment and disposed in special landfills. There is a variety of fly ashes such as Cyclone Fly ash (CF) that is collected by cyclone collectors, Electrostatic Fly ash (EP) that is collected by electrostatic collectors [3].

In landfills, leaching of heavy metals such as nickel and vanadium into ground water, soil, and/or surface water is the main potential environmental concern. Furthermore, due to the limited storage capacity of landfills, safe disposal becomes more and more costly. Current consumption of heavy oil as fuel in power stations in Taiwan is approximately 15 million m$^3$ per year. Based on the statistics, the approximate production of fly ashes is 43000 tons per year that 13000 tons of this amount is EP fly ash and the rest is CY fly ash. Therefore, it is imperative to develop means of both diverting these types of wastes from the solid waste stream, and also recovering nickel and vanadium as valuable metals from fly ashes from environmental and economical viewpoints [3].

Amer [4] leached boiler-ash with sulfuric acid to recover vanadium and nickel sulfate at temperature 200 °C, partial oxygen pressure 15 atm, sulphuric acid concentration 60 g/l. The mentioned process requires high temperature and pressure that is not practical in industrial scale from aspect of economy. In order to extract nickel and vanadium from heavy oil fly ash Tokuyama [5] investigated a process with two different steps; leaching and ion exchange. At leaching process by using water and acid solution Ni, Mg, Al, V and Zn were dissolved and at ion exchange step, more than 80% of V and Ni were recovered on C467 and CR20 ion exchange resins, respectively.

Lai et al [6] studied metals (e.g. Al, Co, Cu, Fe, Mo, Pb, V, and Zn) recovery from spent Hydro Desulfurizarion Catalysts (HDS) by 2 types of strong acids for a leaching period of 0.5-2 h at 70 °C. Metals have been recovered by electrolysis experiments in fluidized-bed electrolytic cell with a nonconductive bed medium. After finding the best condition, the metals recovery for Mo, Ni, V were 14, 60, and 65%, respectively that are not appropriate.

Other scientists have tried to develop a process for extracting and separating both nickel and vanadium from second sources, but most of them have issues such as time-consuming, contaminating ground water and not being cost-effective. On the other hand, some of the suggested routes only work out for vanadium although there was considerable amount of nickel [3, 7-10]. Known secondary sources of nickel and vanadium contain different metals in different amounts. Hence, finding a comprehensive route for extracting and separating these metals have drawn attention of researchers in recent years.

In the present study, solvent extraction has been chosen as one of the best methods for extracting and separating the metals with respect to economy, environmental issues, and also reaching to the point of high separation and extraction. D2EHPA as an extractant, could extract both nickel and vanadium ions relatively but not separately. Although Cyanex 272 is an extractant for extracting and separating both nickel and vanadium with better performance, it is not commercial. Accordingly, a mixture of D2EHPA and Cyanex 272 was studied and discussed. Then, separation factor, as a parameter for determining the separating effect was studied. Finally, the effect of temperature and enthalpy were investigated.

**Experimental**

Each SX test was performed by mixing 200 mL of the aqueous solution with 200 mL of the organic phase. The concentration of the extractant in the organic phase (sole D2EHPA or D2EHPA-Cyanex 272 mixtures) was 0.6 M. The aqueous to organic phase ratio (A/O) of 1:1 was applied in all tests. Experiments were carried out at 25°C. A pH-meter was used to monitor pH during the experiments.

In order to obtain extraction isotherms, pH was successively changed by adding either sulfuric acid or ammonium hydroxide solution drop wise. The two-phase mixture was agitated by a mechanical shaker for approximately 10 minutes. After pH was stable, the phases were allowed to
separate. Then, a sample was taken, transferred to a separatory funnel, and allowed to disengage. The metal ion concentration in the aqueous phase was estimated directly immediately by titration method. The concentration of metal ions in the organic phase was calculated from the difference between concentrations in the aqueous phase before and after extraction by mass balance.

**Results and discussion**

**Effect of increasing Cyanex 272 to D2EHPA on metals extraction**

Cyanex 272 increased to D2EHPA in total fixed 0.6 M extractant, not only for decreasing the co-extraction of nickel, but also for increasing the selectivity in vanadium extraction. Figure 1 illustrates effect of adding Cyanex 272 to D2EHPA on the extraction and separation of vanadium and nickel ions as a function of pH at O/A 1:1 in kerosene at 25°C. This figure demonstrates remarkable synergistic shifts of nickel isotherms to the right in the presence of Cyanex 272, but slight shifts to the left for vanadium isotherms. In other words, addition of Cyanex 272 to D2EHPA substantially improves the separation of V⁴⁺ over Ni²⁺. These results are in contrast with Zhang et al. [11] Gharabaghi et al. [12] and Rodrigues et al. [13]. For scrutinize the best separation, between 0.3 M and 0.45 M of Cyanex 272, two more experiments have been done (0.35 M and 0.4 M of Cyanex 272 at fixed 0.6 M extractants concentration).

![Figure 1. Effect of increasing Cyanex 272 to D2EHPA on extracting nickel and vanadium at 25°C and O/A ratio of 1:1 in kerosene.](image)

As can be seen from Table 1, the ΔpH₀.₅ (difference between pH₀.₅ for vanadium and nickel) varied from 1.5 for 0.6 M D2EHPA to 4.1 for 0.6 M Cyanex 272. Consequently, by using a mixture of Cyanex 272 and D2EHPA, value of the ΔpH₀.₅ is higher than that of sole D2EHPA. Also, the most selective extraction from economical facet for the conditions studied at 25°C can be achieved at D2EHPA to Cyanex 272 volume ratio 0.25 M D2EHPA: 0.35 M Cyanex 272.
Table 1. Values pH_{0.5} for nickel and vanadium and ΔpH_{0.5} (V-Ni) for different mixtures of D2EHPA and Cyanex 272 at 25°C.

<table>
<thead>
<tr>
<th>D2EHPA:Cyanex272</th>
<th>pH_{0.5}</th>
<th>ΔpH_{0.5}(V-Ni)</th>
</tr>
</thead>
<tbody>
<tr>
<td>V</td>
<td>Ni</td>
<td></td>
</tr>
<tr>
<td>0.6:0.0</td>
<td>2</td>
<td>3.5</td>
</tr>
<tr>
<td>0.45:0.15</td>
<td>1.9</td>
<td>4.1</td>
</tr>
<tr>
<td>0.3:0.3</td>
<td>1.8</td>
<td>4.5</td>
</tr>
<tr>
<td>0.25:0.35</td>
<td>1.8</td>
<td>4.7</td>
</tr>
<tr>
<td>0.2:0.4</td>
<td>1.7</td>
<td>5.1</td>
</tr>
<tr>
<td>0.15:0.45</td>
<td>1.6</td>
<td>5.2</td>
</tr>
<tr>
<td>0.0:0.6</td>
<td>1.5</td>
<td>5.6</td>
</tr>
</tbody>
</table>

The distribution coefficient, D, was calculated as the concentration of metal percentage in the organic phase to that part in the aqueous phase at equilibrium. Accordingly, separation factor (β_{V/Ni}) can be calculated by dividing D value of each metal to another one. The results of the distribution coefficient values and separation factor calculation are shown in table 2.

Table 2. Values of D_V, D_Ni and β_{V/Ni} for different mixtures of D2EHPA with Cyanex 272.

<table>
<thead>
<tr>
<th>Molar ratio of D2EHPA: Cyanex 272</th>
<th>D_V</th>
<th>D_Ni</th>
<th>β_{V/Ni}</th>
<th>pH1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.60:0.00</td>
<td>0.369</td>
<td>0.111</td>
<td>3.328</td>
<td></td>
<td>0.400</td>
<td>0.360</td>
<td>0.333</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>3.444</td>
<td>5.666</td>
<td>2.773</td>
<td>2.043</td>
</tr>
<tr>
<td>0.45:0.15</td>
<td>0.298</td>
<td>0.092</td>
<td>3.215</td>
<td></td>
<td>1.325</td>
<td>4.882</td>
<td>7.333</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3.250</td>
<td>5.666</td>
<td>9.000</td>
<td>11.86</td>
</tr>
<tr>
<td>0.30:0.30</td>
<td>0.250</td>
<td>0.077</td>
<td>3.222</td>
<td></td>
<td>1.500</td>
<td>5.666</td>
<td>9.000</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>5.666</td>
<td>9.000</td>
<td>11.86</td>
<td>24.96</td>
</tr>
<tr>
<td>0.25:0.35</td>
<td>0.219</td>
<td>0.054</td>
<td>4.001</td>
<td></td>
<td>1.857</td>
<td>7.333</td>
<td>13.28</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>7.333</td>
<td>13.28</td>
<td>20.70</td>
<td>107.4</td>
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<tr>
<td>0.20:0.40</td>
<td>0.190</td>
<td>0.049</td>
<td>3.862</td>
<td></td>
<td>2.333</td>
<td>7.333</td>
<td>13.70</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>7.333</td>
<td>13.70</td>
<td>20.70</td>
<td>123.3</td>
</tr>
<tr>
<td>0.15:0.45</td>
<td>0.162</td>
<td>0.033</td>
<td>4.924</td>
<td></td>
<td>3.000</td>
<td>13.28</td>
<td>19.00</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>13.28</td>
<td>19.00</td>
<td>20.70</td>
<td>218.5</td>
</tr>
<tr>
<td>0.00:0.60</td>
<td>0.092</td>
<td>0.020</td>
<td>4.551</td>
<td></td>
<td>3.444</td>
<td>13.28</td>
<td>19.00</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>13.28</td>
<td>19.00</td>
<td>218.5</td>
<td>218.5</td>
</tr>
</tbody>
</table>

Separation factor indicates how extractant efficiently can separate nickel from vanadium. Figure 2 depicted the separation factors of various proportions of D2EHPA to Cyanex 272 at different pHs. It is obvious that by increasing the Cyanex 272 to D2EHPA separation factor increased. At first stages of increasing Cyanex 272, it had a minor influence, but after 0.3M adding Cyanex 272 to D2EHPA it began to make its significant influence more and more as can be seen in...
the Figure. Maximum separation factor was obtained at pH 4 by sole Cyanex 272 ($\beta=218.5$). Since Cyanex 272 is more expensive than D2EHPA, using sole Cyanex 272 was not cost-effective. Thus, the ratio of 0.25M D2EHPA to 0.35M Cyanex 272 was chosen as the best ratio.

Figure 2. Separation factor vs. equilibrium pH with sole D2EHPA, mixtures of D2EHPA to Cyanex 272, and sole Cyanex 272.

**Effect of temperature on nickel and vanadium extraction**

To evaluate the effect of temperature, extraction isotherms of vanadium and nickel at 35, 45, and 55 °C were determined for a 0.35 M:0.25 M mixture of Cyanex 272:D2EHPA diluted in kerosene at O/A ratio of 1:1. These are shown in Fig. 3 alongside with the corresponding isotherms at 25 °C for comparison. Generally, the extraction of vanadium increases slightly as the temperature increases from 25 °C to 55 °C. Extraction of nickel also increases with increasing temperature from 25°C to 55 °C. It can be concluded both extraction isotherms are shifted to the left, but not to the same extent towards pHs by increasing the temperature. Extraction isotherm for nickel is shifted to the left more than vanadium; it indicates that higher temperatures are not beneficial for the separation of nickel and vanadium.

Figure 3. Effect of temperature on the extraction of vanadium and nickel using 0.25 M D2EHPA and 0.35 M Cyanex 272 and A/O ratio of 1:1.
The influence of temperature has been studied in the present work for vanadium and nickel extraction at pH 2 and 4.5, respectively at fixed concentrations of D2EHPA and Cyanex 272 (D2EHPA=0.25 M, Cyanex 272=0.35 M) in a synergistic system. The relationship between distribution ratio and temperature is explained as equation (1). By achieving distribution ratio and temperature, the change of enthalpy of the reaction, $\Delta H$, can be calculated.

$$\frac{\Delta \log D}{\Delta \left(\frac{1}{T}\right)} = -\frac{\Delta H}{2.303 R}$$  \hspace{1cm} (1)

Plot of log $D$ versus $T^{-1}$ (K$^{-1}$) for vanadium and nickel are shown in Fig. 4 and 5, respectively. The $\Delta H$ value was calculated for vanadium as 12.12 kJ mol$^{-1}$ and also for nickel calculated as 20.72 kJ mol$^{-1}$.

![Figure 4](image1.png)

**Figure 4.** Relationship between distribution coefficient and temperature for vanadium extraction, pH = 2.

The sign of $\Delta H$ for both metal ions are positive, indicating that synergistic extraction process is endothermically driven. These results are comparable with Li et al. [14] and Darvishi et al. [15] work.

![Figure 5](image2.png)

**Figure 5.** Relationship between distribution coefficient and temperature for nickel extraction, pH = 4.5.
Conclusions

- Increasing Cyanex 272 to D2EHPA at fixed total concentration of 0.6M for extraction of vanadium and nickel from sulfate media affect a slight shift to the left on extraction isotherm of vanadium, but a major influence on nickel extraction by shifting isotherm to the right.
- Separation factor by using sole Cyanex 272 extractant is 218.5 that is the maximum proportion.
- Increasing the temperature from 25 to 55°C shifted both nickel and vanadium extraction isotherms to the left both not in the same extend and aggravate the separation of both metals.
- Change of enthalpy, ΔH, was determined for vanadium and nickel, 12.12 kJ mol⁻¹ and 20.72 kJ mol⁻¹, respectively.

References


