Separation and Purification Technology 136 (2014) 265–273

Contents lists available at ScienceDirect

Separation and Purification Technology

journal homepage: www.elsevier.com/locate/seppur

Selective recovery and separation of nickel and vanadium in sulfate media using mixtures of D2EHPA and Cyanex 272

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ARTICLE INFO

Article history:
Received 14 May 2014
Received in revised form 23 August 2014
Accepted 30 August 2014
Available online 19 September 2014

Keywords:
Nickel
Vanadium
D2EHPA
Cyanex 272
Separation
Solvent extraction

ABSTRACT

In this research, selective recovery and separation of nickel and vanadium in sulfate media was investigated by solvent extraction using D2EHPA, Cyanex 272, and their mixtures in various proportions. For this purpose, synthetic sulfate solutions of nickel and vanadium were prepared in 2 g/L of each metal. After dilution of the organic solvents in kerosene with the ratio of 1–4, experiments were carried out in the pH range of 1.0–7.0 in steps of 0.5 at ambient temperature. Solvent extraction of nickel and vanadium by sole D2EHPA was performed and the extraction percentages were 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_{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 simultaneous separation of nickel and vanadium. 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; thus, 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 and various temperatures (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_{50} values for nickel and vanadium were shifted from 3.5 to 4.75 and from 2 to 1.75, respectively.

1. 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. On the other hand, fulfilling of burned or spent materials which contains toxic metals could leave irreparable environmental effects. In recent years, various secondary sources of vanadium and nickel such as fly ashes, crude oil, power plants residues, spent catalysts and stone coals have drawn attention of researchers to recovery of metals [1–4].

Fly ash generated by power plants is categorized as a special waste by US EPA. There are variety of fly ashes such as Cyclone Fly ash (CF) which is collected by cyclone collectors and Electrostatic Precipitated fly ash (EP) which is captured by electrostatic collectors. These residues from fossil fuel combustion are captured by pollution control equipment and disposed in special landfills. The mentioned fly ashes are very fine and due to their low density, proper disposal of them is very difficult [5,6].

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. Additionally, due to the limited storage capacity of landfills, safe disposal becomes more and more costly. Based on the statistics, the annual production of fly ash from coal-fired power plants (CFP) in Europe is almost 38 million tons. Furthermore, incinerators generate about 12 million tons of fly ash annually from 250 million tons of municipal solid wastes in Europe [7]. In Taiwan, the approximate production of fly ashes is 43,000 tons per year that 13,000 tons of total amount is EP fly ash and the rest is CY fly ash [6]. Also, The fraction of vanadium-containing fuel oil in power generation plant production at domestic thermal power stations in Russia is 13%; this corresponds to around 7 million tons per year [8]. 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

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http://dx.doi.org/10.1016/j.seppur.2014.08.038
1383-5866/

valuable metals from fly ashes due to environmental and economic reasons.

Hence, in order to find a comprehensive route for extracting and separating nickel and vanadium, researchers have paid special attention to this subject in recent years. Different hydrometallurgical processes (leaching, ion exchange, electrolysis, cementation, precipitation, crystallization, and solvent extraction) have been used to recover and separate metals from each other [9]. Solvent extraction as one of the environmentally friendliest processes, is a hydrometallurgical method for purification, concentration, and separation of metals from each other [10,11]. Solvent extraction of nickel and vanadium was studied by using D2EHPA, Cyanex 272, Cyanex 923, Cyanex 302, and PC88-A as a synergist system or sole extractant for evaluating the separation and extraction of the metals in chloride and sulfate media [12–26].

In order to extract nickel and vanadium from secondary sources different hydrometallurgical routes have been used by researches. Kersch et al. [7] studied extraction of heavy metals from fly ash by supercritical CO_2 fluid and solvent extraction. Amer [27] leached boiler-ash with sulfuric acid to recover vanadium and nickel. Lai et al. [28] studied metals (e.g., Al, Co, Cu, Fe, Mo, Pb, V, and Zn) recovery from spent Hydro Desulfurization Catalysts (HDS) by electrolysis experiments. To recover Ni and V, acidic leaching of power plant fly ash which contains Ni, V, Mn, Fe, Cr, Mg, Zn, Pb, and Al was performed by Nazari et al. [29]. Except for nickel, vanadium and iron, concentration of other elements in the fly ash was less than 1%; therefore, the mentioned elements made no major influences on solvent extraction process. In addition, since Fe^{2+} is not extractable by D2EHPA and Cyanex 272 [19,30], to control iron concentration during the solvent extraction process, iron can be reduced from Fe^{3+} to Fe^{2+}. In order to extract nickel and vanadium from heavy oil fly ash, Tokuyama et al. [31] investigated a process with two different steps; leaching and ion exchange. Al-Ghouti et al. [32] studied extraction and separation of vanadium and nickel from fly ash produced in heavy fuel plants. Although researchers have tried to develop a process for extracting and separating both nickel and vanadium from secondary sources, they ended up with problems such as being time-consuming, contaminating ground water, producing degraded salts, operating non-selective, and not being cost-effective. On the other hand, some of the suggested routes only work out for vanadium; although, there were considerable amount of nickel or vice versa [1,5,33–35].

Instead of using a single extractant, mixtures of extractants can give rise to synergistic effects and better selectivity of metal extraction/separation in solvent extraction processes [16–22,36–38]. Previously, synergism has been applied to the separation of nickel–cobalt system by Darvishi and his co-workers. Using D2EHPA, Cyanex 272 and Cyanex 302, Babakhani et al. also studied synergism for separating nickel and cadmium from sulfate media by using mixtures of D2EHPA and Cyanex 302 [22]. In order to separate valuable metals such as cobalt, copper, manganese, and lithium from leach liquors of lithium ion batteries, mixtures of PC-88A and Cyanex 272 and their synergistic effects have been studied [39,40]. Also, influence of TBP as both an organophosphorus extractant [19,41–44] and a modifier [22,45] on solvent extraction systems has been investigated by various researchers. It is worth mentioning that TBP as a modifier could avoid the third phase formation and enhance separation factor during solvent extraction processes.

In the present study, solvent extraction has been used for extraction and separation of vanadium and nickel from sulfate solution. As a commercial extractant, D2EHPA has been used for extracting nickel and vanadium, despite the fact that D2EHPA has a co-extraction property [16,19,22,24,25,46] . Therefore, using sole D2EHPA is unacceptable for this purpose. Among cationic extractants Cyanex 272 shows better features of extraction on V (IV) and nickel (II) in sulfate medium while Cyanex 923 and 921 are suitable for chloride medium [14,16,25,46,47]. In addition, Cyanex 302 completed extraction of vanadium (IV) at pH 5 and Cyanex 301 extracts nickel and vanadium at nearly same pHs [48,49]. Although Cyanex 272 offers proper extraction and separation for both nickel and vanadium, it is relatively more expensive to be used commercially. Thus, for the commercial application aims,

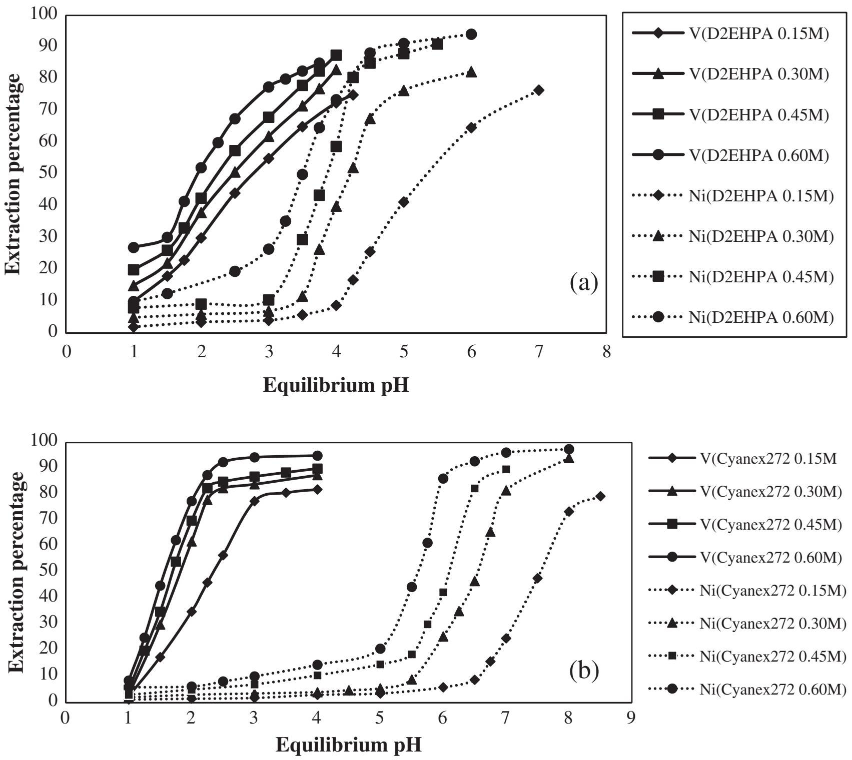

Fig. 1. Extraction of vanadium and nickel as a function of pH at 25 °C and *O*/*A* ratio of 1:1 in kerosene, (b) Cyanex 272.