Hydrometallurgy 147–148 (2014) 142–147

Contents lists available at ScienceDirect

Hydrometallurgy

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

Technical note

Recovery of molybdenum and vanadium with high purity from sulfuric acid leach solution of spent hydrodesulfurization catalysts by ion exchange

Thi Hong Nguyen, Man Seung Lee *

Department of Advanced Material Science & Engineering, Institute of Rare Metal, Mokpo National University, Chonnam 534-729, Republic of Korea

ARTICLE INFO

Article history:
Received 15 October 2013
Received in revised form 13 May 2014
Accepted 15 May 2014
Available online 3 June 2014

Keywords:
Molybdenum
Vanadium
Sulfuric acid
Ion exchange
AG1-x8

ABSTRACT

Valuable metals, such as Mo, V, Co and Ni together with base metals (Fe and Al) are present in the sulfuric acid leaching solutions of spent hydrodesulfurization catalysts. In order to develop a process to recover pure Mo and V from the solution, batch and continuous ion exchange experiments with strong anionic resin (AG1-x8) have been performed by employing a synthetic sulfuric acid solution. Batch experimental results indicated that the separation of molybdenum and vanadium from the solution with AG1-x8 was possible by adjusting the pH of the solution to 0.5 and 1.6, respectively. Column experimental results verified the complete separation and recovery of molybdenum and vanadium from the solution at the specified pH conditions. Molybdenum and vanadium in the loaded resin was eluted by using NaOH solution. The purity of Mo and V solution after elution was found to be higher than 99%. After elution, AG1-x8 was successfully regenerated by converting its form from hydroxide to chloride by using NaCl solution.

1. Introduction

In spent hydrodesulfurization (HDS) catalysts, valuable rare metals, such as Mo, V, Co and Ni are present. Since the mineral ores containing these metals become depleted, the recovery of these metals from spent HDS catalysts is attractive (Park et al., 2006). In hydrometallurgical treatment of the spent HDS catalysts, roasting followed by water leaching or acidic leaching step is employed to dissolve the metals to be recovered (Chen et al., 2006; Kar et al., 2004; Toda and Morimoto, 1983; Toda et al., 1979). In the former case, the spent HDS catalysts are roasted at 600–800 °C with Na_2CO_3, which converts the Mo and V in the spent catalysts into sodium compound. These sodium compounds of Mo and V are easily dissolved in hot water, while Co and Ni remain in the residue. In the sulfuric acid leaching process, all the valuable metals (Mo, V, Co and Ni) can be dissolved in one step. Moreover, sulfuric acid leaching process has several advantages, such as more flexibility in the choice of materials for construction of reactor, lower cost and better recirculation possibilities (Mishra et al., 2010; Zeng and Cheng, 2009a). Not only valuable metals (Mo, V, Co, Ni) but also some base metals (Fe, Al) coexist in the sulfuric acid leach solutions of the spent HDS catalysts (Zeng and Cheng, 2010). Therefore, in order to produce the metallic compound of each valuable metal, the metal ions in the leaching solution should be separated from each other.

Ion exchange (Hu et al., 2009; Li et al., 2009; Nguyen and Lee, 2013a; 2013b; Wang et al., 2010) and solvent extraction (Zeng and Cheng, 2009b, 2010; Zhang et al., 1996) are generally employed to separate metal ions present in aqueous solution. In these two processes, each has its advantages and disadvantages over the other. First, solvent extraction is highly selective and efficient for the extraction of Mo and V from sulfuric acid leach solution. However, owing to the co-extraction of Co, Ni, Fe and Al during the extraction of Mo and V, separation of Mo and V is not complete in extraction alone (Zeng and Cheng, 2010; Zhang et al., 1996). Although the loading capacity of ion exchange for metal ions is generally low, operation of ion exchange is simple and production of Mo and V with high purity is possible. Hence, when the concentration of Mo and V in sulfuric acid solution is not high, ion exchange resins can selectively load Mo and V from the solution in the presence of other metals.

Anionic species of Mo is formed when the solution pH is higher than 0.5, while that of V is formed at pH > 1.0 (Hu et al., 2009; Zeng and Cheng, 2009b). Thus, anionic resins can be used to separate Mo from V in the pH range from 0.5 to 1.0. In our previous studies on the separation of Mo and V, it was found that separation of Mo and V from acidic solution is possible (Nguyen and Lee, 2013a). Moreover, presence of Co and Ni in the acidic solution was found to have negligible effect on the separation of Mo and V (Nguyen and Lee, 2013a). In hydrochloric acid solution, Mo can be separated from Co and Fe, when solution pH is higher than 1.0 (Nguyen et al., 2013). In this condition, Co and Fe are not loaded into AG1-x8. Consequently, AG1-x8 can be regarded as a promising resin for effective separation and recovery of Mo and V from acid leaching solution containing Co, Ni and Fe.

However, little information has been found regarding not only the separation efficiency of Mo and V from real leaching solution containing

---

* Corresponding author. Tel.: +82 61 450 2492; fax: +82 61 450 2498.
E-mail address: mslee@mokpo.ac.kr (M.S. Lee).

http://dx.doi.org/10.1016/j.hydromet.2014.05.010
0304-386X/

Co, Ni, Fe and Al with AG1-x8, but also the effective elution of these metals from the loaded resin. In our previous studies, the possibility of separating Mo and V in presence of Co and Ni was verified by batch experiments (Nguyen and Lee, 2013a). However, there was no data about the continuous experiments by using AG1-x8 and about the effect of iron on the separation efficiency of Mo and V.

In the present study, particular attention has been given to the column experiments for the separation and elution of Mo and V from a sulfuric acid leaching solution of spent catalyst with AG1-x8. For this purpose, a synthetic sulfuric acid solution of spent HDS catalysts was employed in the ion exchange experiments. The loading capacity of AG1-x8 for Mo and V at the optimum loading condition was determined. The recovery percentage of Mo and V from the sulfuric acid leaching solution and the purity of these metals after column experiments is reported.

2. Experimental

2.1. Chemicals and resin

AG1-x8 (Bio-Rad) is a strong basic anion exchanger with quaternary ammonium functional groups attached to the styrene divinylbenzene copolymer lattice. The physicochemical properties of AG1-x8 resin are listed in Table 1. AG1-x8 resin was in the chloride form (RCl) and it is used as received without any treatment in the current study.

The sulfuric acid leaching solution of spent HDS catalysts contain Mo, V, Co, Ni, Fe and Al (Zeng and Cheng, 2010). In this study, a synthetic sulfuric acid leaching solution was employed in ion exchange experiments. Since aluminum is not loaded into AG1-x8 in the acid concentration range from 1 to 6 M and does not affect the loading behavior of other metal ions (Nguyen and Lee, 2013b), aluminum was not included in the preparation of the synthetic sulfuric acid solution. The synthetic sulfuric acid solution was prepared by dissolving the chemicals of molybdenum, vanadium, nickel, cobalt and iron in doubly distilled water. The concentration of these metals in the solution is shown in Table 2. H_2SO_4 solution was added to adjust the acidity of the synthetic solution. All the chemicals used in this study were of analytical reagent grade.

2.2. Ion exchange procedure

Loading experiments were carried out by putting some amount of resins into 10 mL synthetic solution. The samples were shaken in a shaking incubator (HB-201SF, Hanbeak Scientific Co.) for 24 h at room temperature. After filtering the resin by filter papers, the concentration of metals in the solution was measured by using ICP-OES (Spectro Arcos). The concentration of metal loaded into resin was obtained by mass balance. Adsorption percentage of metals was calculated by Eq. (1).

$$\text{Adsorption\%} = \frac{\text{Difference of the metal concentrations before and after the loading}}{\text{Concentration of metal in the feed}} \tag{1}$$

In column experiments, a glass column (250 × 10 mm) was used. After some amount of resin was poured into the column, the operation was performed at a constant flow rate of 1.5 mL/min. Flow rate of the solution was controlled by using a pump (QG20 lab pump, FMI). The effluent was fractionated into portions of desired volume and the concentration of metals in each fraction was measured. The cumulative amount of the metal loaded into the resin was calculated by the difference in the concentration of metal in each fraction.

Table 1
Physicochemical characteristics of AG1-x8 used in this study.

Resin	Ionic forms	Dry mesh size	Bead size (μm)	Density (g/mL)
AG1-x8	Chloride	200–400	45–106	0.75

Table 2
The chemical composition of a synthetic sulfuric acid leaching solution of spent HDS catalysts and chemicals used in preparing the solutions (Zeng and Cheng, 2010).

Element	Chemical	Concentration (mg/L)
Mo	$MoNa_2O_4$	2800
V	Na_3O_4V	910
Ni	$NiSO_4 \cdot 6H_2O$	470
Co	$CoSO_4 \cdot 7H_2O$	949
Fe	$Fe_2(SO_4)_3 \cdot 6H_2O$	239

3. Results and discussions

3.1. Batch experiments

3.1.1. Effect of solution pH

In order to investigate the effect of solution pH on the loading of metals from sulfuric acid leaching solution, experiments were carried out in the solution pH range from 0.5 to 1.8. The concentration of Mo, V, Ni, Co and Fe in sulfuric acid solution was 2800 mg/L, 910 mg/L, 470 mg/L, 949 mg/L and 293 mg/L, respectively. The concentration of AG1-x8 in the solution was kept at 10 g/L and the results are shown in Fig. 1. The loading percentage of molybdenum declined gradually from 73 to 50% with the increase of solution pH from 0.5 to 1.8, while that of vanadium rose rapidly from zero to 74%. However, the loading percentage of Co, Ni and Fe was negligible in our experimental range. This result agrees well with our previous results reported in the literature (Nguyen and Lee, 2013a). Fig. 1 indicates that it is possible to separate Mo from the sulfuric acid solution containing V, Co, Ni and Fe by ion exchange with AG1-x8 resin as long as the solution pH is maintained at around 0.5. Since the loading percentage of Co, Ni and Fe was nearly zero in our experimental range, it can be inferred that no anionic species of Co, Ni and Fe is formed in our experimental range. Compared to our previous results, the presence of iron in the solution seems to have a negligible effect on loading of Mo and V with AG1-x8.

The loading behavior of Mo and V by AG1-x8 in the pH range from 0.5 to 1.8 may be explained by the nature of predominant species of each element. It has been reported that anionic species of $H_2V_{10}O_{28}^{4-}$ is predominant at pH > 1.0 (Hu et al., 2009). According to the distribution diagram of molybdenum in aqueous solution, the predominant species

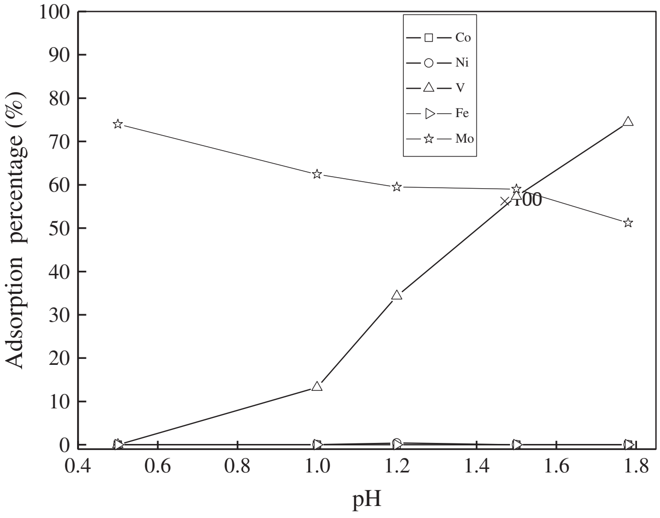

Fig. 1. Effect of solution pH on the loading of the metal ions from sulfuric acid solution with 10 g/L AG1-x8 at room temperature. Feed solution, mg/L: Mo-2800; V-910; Co-949; Ni-470; Fe-239.