Recovery of Molybdenum from the Deep Sea Manganese Nodules

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ABSTRACT

Molybdenum is one of significant refractory metals used as an alloying agent in cast iron, steel and super alloys and in numerous chemical applications including catalysts, lubricants and pigments. Due to its increasing demand of molybdenum and rapid depletion of its land based ores, there is a growing need to find alternate sources to meet the future demands. Manganese nodule contains about 0.05% molybdenum and is one of candidates. Separation and recovery of molybdenum was carried out from the sea nodule leach liquor containing 0.505 kg/m^3 Mo(VI), 0.212 kg/m^3 Fe(III), 12.08 kg/m^3 Cu(II), 2.012 kg/m^3 Co(II) and 15.16 kg/m^3 Ni(II). The recovery process was carried out in two key steps such as: (i) Solvent extraction of Mo(VI) using Alamine 304-1 dissolved in kerosene of leach liquor and stripping, and (ii) Preparation of MoO_3 by crystallization and thermal decomposition of stripped solution. By this process, MoO_3 with purity of 99.4% can be obtained.

KEY WORDS: Sea nodule; recovery; molybdenum; solvent extraction; crystallization.

INTRODUCTION

There is an extensive demand of pure molybdenum in the industrial applications like the production of ferro-molybdenum in special steel making process. The major use of molybdenum is in the petrochemical refining processes, where it is used as a catalyst. Nonetheless, it is also considered as one of the important constituent of anticathode of X-ray tubes, pigments and lubricants (Sailly-Khurana-Yadav and Tandon, 1996; Sutlov, 1979). Due to the growing need of such metals with high purity and the rapid depletion of land based ores, that has necessitated for exploitation of alternate sources to meet the future demand. Vast oceans are such primary sources which claimed to have major constituents like manganese (27-30 %), nickel (1.25-1.5 %), copper (1-1.4 %) and cobalt (0.2-0.25 %), along with a minor content of molybdenum (~0.05%) (Fuertuenau and Han, 1977).

Over last three decades lots of efforts has been put foreword to develop a successful flow sheet by pyrometallurgical, hydrometallurgical or pyro-hydrometallurgical route to recover the metal values from manganese nodules (Fuertuenau and Han, 1983). The processing of Pacific Ocean manganese nodule for recovery of valuable metals functioning at Korea Institute of Geoscience & Mineral Resources (KIGAM) follows pyro-hydrometallurgical route (Nam-Kim and Park, 2003). On reductive roasting and smelting of the manganese nodule produces a Cu-Ni-Co-Fe matte with a minor content of Mo, which was subjected for oxidative pressure leaching with dilute sulphuric acid for selective extraction of Cu, Co, Ni and Mo leaving the major percentages of Fe in the residue (Nam-park and Kim, 2004). This leaching solution produces 0.2 kg/m^3 Fe(III), 0.5 kg/m^3 Mo(VI), 12 kg/m^3 Cu(II), 2 kg/m^3 Co(II) and 15 kg/m^3 Ni(II) with solution pH-2.0. Molybdenum concentration in leach liquor is relatively low as compared to the other metals and limited studies are reported for its recovery (Monhemius, 1986). However, this low molybdenum content of the leach liquor can be enriched to a desired concentration by solvent extraction process and hence the present work was undertaken to investigate the selective solvent extraction and its recovery from the sea nodule leach liquor.

Several authors have studied the extraction of molybdenum from the aqueous solutions by various hydrometallurgical techniques such as: Ion exchange (Chen-Kao and Lin, 2003), supported liquid membrane separation (Marchese-Valenzuela-Basualto and Acosta, 2004), precipitation (Warren and Reid, 1982) and solvent extraction (henceforth abbreviated as SX) (Zhang-Inoue-Yoshizuka and Tsuyama, 1996; An-Lee-Kim- Tran-Lee and Kim, 2009a) and each of the techniques has its own advantages and disadvantages. Of these techniques, solvent extraction is apparently an important in recent years as a promising industrial process in extraction and separation of molybdenum from the various aqueous leach solutions containing the other metal ions such as Cu, Co, Fe, Al and Ni (Taich-Hiroshi and Hiroki, 1986; Valverde Jr- Paulino and Afonso,, 2008).

A considerable amount of work has been devoted for the recovery of molybdenum from aqueous solution by solvent extraction using various organic extractants such as amines (Marchese-Valenzuela-Basualto and Acosta, 2004; Mons-Diez, and Coca, 1999; Mohammad-Yunus-Haron, and Rahman, 2008), oximes (Kim-Park and Parhi, 2010; Zhang-Inoue-Yoshizuka and Tsuyama, 1996), organo-phosphorous groups (Cheng-Lee-Chen and Ting, 1989; Valenzuela-Andrade-Sapag-Tapia and Basualto, 1995; Sato-Watanabe and Suzuki, 1986), and thiophosphinic acid group (Saberyan-Maragheh and Ganjali, 2004), respectively.

From the above literature survey, most of the extractants namely phosphoric and thiophosphoric acid, oximes and amines, are being applied for solvent extraction of molybdenum from acidic solutions bearing other base metals such as Al, Ni, Co, of various secondary sources (Behera-Mishra-Mohanty and Chakravortty, 1994; Lee-Kumar-Jeon and Kim, 2010). In contrast, a few attempts have been made relating to the extraction of molybdenum from the acidic leach solutions which invariably contains the impurities like Cu and Fe (An, 2009a; Valenzuela-Andrade-Sapag-Tapia and Basualto, 1995; Gerhardt-Palant-Petrova and Tagirov, 2001) and from the results it was observed that the selectivity of metal extraction was controlled by adjusting the pH of the respective solution to a desired value. Moreover, the reagent: Trilauryl amine (Alamine 304-1) which is chosen as the extractant for the current investigation, found to be highly selective and