Journal of Hazardous Materials 318 (2016) 24–31

Contents lists available at ScienceDirect

Journal of Hazardous Materials

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

Re-manufacture of cobalt-manganese-bromide as a liquid catalyst from spent catalyst containing cobalt generated from petrochemical processes via hydrometallurgy

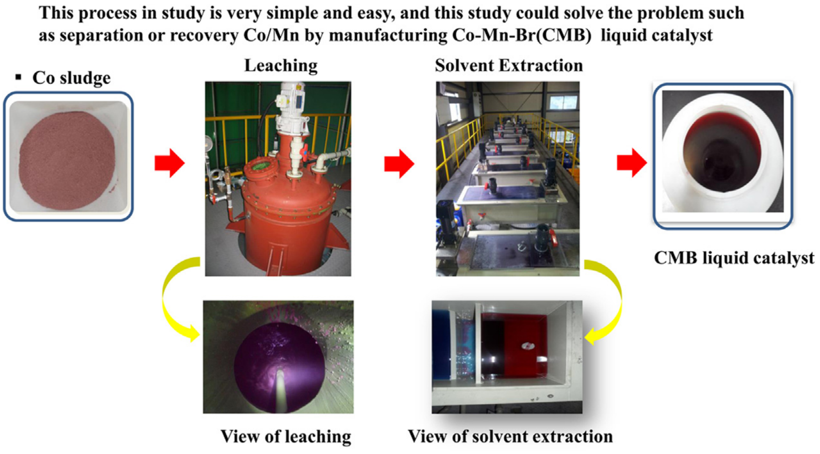
Sung-Ho Joo[a,b], Dong Ju Shin[b], Chang Hyun Oh[b], Jei-Pil Wang[c], Shun Myung Shin[a,b,*]

[a] Department of Resource Recycling, Korea University of Science & Technology (UST), Republic of Korea
[b] Department of Extractive Metallurgy, Korea Institute of Geoscience & Mineral Resources (KIGAM), Republic of Korea
[c] Department of Metallurgical Engineering, Pukyong National University, Republic of Korea

HIGHLIGHTS

- A spent CMB catalyst was completely leached at 1 M H_2SO_4, 40 °C and 0.1 of S/L ratio.
- The S × F value of Co and Mn over Ca and Mg was higher than 11 by Na-Cyanex 272.
- Co and Mn was recovered from Ca and Mg through 4 stage extraction by Na-Cayenx 272.
- Re-manufactured CMB contains 48.5 g/L Co and 23.2 g/L Mn by 2 M HBr in stripping.
- In pilot plant, 288 L CMB liquid catalyst could be produced during 24 h.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 25 March 2016
Received in revised form 2 June 2016
Accepted 4 June 2016
Available online 6 June 2016

Keywords:
Cobalt
Manganese
Hydrogen bromide
Na-bis-(2,4,4-tri-methyl-pentyl)phosphinic acid

ABSTRACT

Cobalt and manganese have been the subject of individual separation studies because their fields of application are different. However, this study shows that high-value products can be manufactured in the form of a cobalt-manganese-bromide (CMB) liquid catalyst by simultaneously recovering cobalt and manganese. Na-bis-(2,4,4-tri-methyl-pentyl)phosphinic acid was employed in order to manufacture the CMB liquid catalyst from the spent catalyst generated from petroleum chemistry processes. The pH-isotherm, degree of saponification of solvent and separation factor values were investigated. ΔpH_{50} and separation factor values show that Co and Mn can be separated from impurities such as Mg and Ca. Further, the extraction stages and organic/aqueous ratio isotherms were investigated using counter-current simulation extraction batch tests. To prepare CMB from a loaded organic phase obtained in a stripping study using hydrogen bromide, the Co and Mn were completely stripped and concentrated by a factor of 6 using a 2 M hydrogen bromide solution. When compared with manufactured

---

* Corresponding author at: Department of Extractive Metallurgy, Korea Institute of Geoscience & Mineral Resources (KIGAM), Deajeon 305-350, Republic of Korea.
E-mail address: shin1016@kigam.re.kr (S.M. Shin).

http://dx.doi.org/10.1016/j.jhazmat.2016.06.008

and commercial CMB, the CMB liquid catalyst could be produced by supplying a shortage of Mn in the form of manganese bromide. Finally, the method of manufacture of CMB was subjected to a real pilot plant test.

1. Introduction

Many researchers have been interested in the recovery of cobalt from secondary resources such as spent catalysts or Li-ion batteries containing cobalt because of the economic value of cobalt and from an environmental perspective considering cobalt toxicity. However, spent catalysts or Li-ion batteries contain not only Co but also Mn and other metals. It follows that individual separation and recovery of Mn and Co are not easy because their physical and chemical behaviors are similar.

The acid extractants typically employed in hydrometallurgy, such as di-(2-ethylhexyl)phosphoric acid (D2EHPA), bis-(2,4,4-tri-methyl-pentyl)phosphinic acid (Cyanex 272) and 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC88A), preferentially extract manganese rather than cobalt [1–5]. Therefore, after recovering manganese, cobalt is extracted and recovered from the manganese-free solution. However, reported studies have shown that separation of Mn from Co is difficult due to the small difference in their pH_{50} values [6,7]. Of course, mixed acid extractants, such as PC88A/monocarboxylic acid (Versatic 10 acid) and D2EHPA/Versatic 10 acid, have increased the separation factor values of manganese over cobalt [8–10], however, mixed acid extractants is laboratory experiment data, also, not yet to be applied to commercial process. Conversely, other extractants, such as bis(2,4,4-trimethylpentyl)dithiophosphinic acid (Cyanex 301), which preferentially extracts cobalt over manganese, are expensive [11,12]. Studies that have reported synergistic effects used mixtures of extractants such as the versatic 10 acid and LIX-type extractants [13,14]. The studies reporting synergistic effects reported preferential extraction and increased pH_{50} values for cobalt over manganese. However, these studies also reported problems such as stripping rate, use of TBP and coping method for solvent loss. Another process for the separation of manganese and cobalt is the precipitation method. SO_2/O_2 gas selectively precipitates Mn in the form of MnO_2 from cobalt and nickel at low pH [15]. Similarly, chemicals such as $Na_2S_2O_8$ or $(NH_4)_2S_2O_8$ precipitate Mn in the form of MnO_2 [16,17]. Although the aforementioned methods of precipitation are efficient, real plants may not prefer precipitation methods because precipitants are expensive and the product manufactured, MnO_2, is inexpensive. The aforementioned studies have reported individual separation of cobalt and manganese. From an economic point of view, most researchers are likely interested in methods of manufacturing high-purity cobalt salts and cobalt metal or manganese salts and manganese oxide. Therefore, if individual separation of cobalt and manganese is not completely achieved, the stages in the separation and purification process must be increased because cobalt and manganese are each considered to be impurities in the other. If a high-value product is manufactured without separation of cobalt and manganese by simultaneously recovering both cobalt and manganese, this process may decrease the loss of metals during the process of separation and purification. This also has direct economic impacts. These problems can be solved by manufacturing cobalt-manganese-bromide (CMB) liquid catalysts as alternative of treating Co wastes.

CMB liquid catalysts containing cobalt, manganese and bromine are used for the catalytic oxidation of *para*-xylene (PX), a petrochemical, to terephthalic acid (TPA) and di-methyl terephthalate (DMT). The process is catalyzed homogeneously using manganese-containing cobalt acetate or bromide [18]. The manufacture of TPA uses a catalyst with a Co:Mn ratio of 1:3, while the DMT catalyst has a higher Co:Mn ratio (10:1). TPA and DMT are raw materials for products indispensable to our daily life, such as polyester fibers, polyethylene terephthalate (PET) bottles, films, paints and tire cords. South Korea, a major TPA supplier, produced 2.281 thousand tons of TPA in 2014. South Korea, Taiwan, Thailand and Mexico make up approximately 94% of the global TPA production capacity [19]. According to our own investigations, the spent CMB generated after the manufacture of TPA or DMT is reused following a precipitation and incineration process. However, this results in poor quality of the manufactured product. Alternatively, the spent CMB is recovered by precipitation and flown out to another country, or it is discarded in landfills in Korea. The outflow and disposal in landfills are both economic and environmental concerns due to the presence of cobalt in the spent CMB. Therefore, the aim of this study is the re-manufacture of CMB liquid catalysts as a high-value product that can be manufactured from spent CMB catalyst precipitates without the separation of Co from Mn.

2. Materials and methods

2.1. Materials and regents

The sample, which was precipitated through a series of processes, was kindly supplied by the CMB manufacture plant in Korea (Fig. 1). As seen from the XRD analysis in Fig. 2, the sample is a carbonated powder. The composition of valuable metals in the sample is given in Table 1.

The commercial extractant bis(2,4,4-trimethylpentyl)phosphinic acid (Cyanex 272) was supplied by Cytec Inc. and was used without further purification. Commercial grade extra-pure kerosene (bp 180–270 °C) (Junsei Chemicals Co. Ltd., Japan) was used as a diluent for all sets of experiments. HBr (Sigma-Aldrich, USA) was utilized as a stripping solution for solvent extraction.

2.2. Method and procedure

To prepare the feed solution, leaching tests were conducted at different concentrations of H_2SO_4 and temperature, maintaining a solid/liquid ratio of 0.1. To determine the valuable metals extracted, pH isotherm tests were conducted at room temperature and different pH values with Cyanex 272, an O/A ratio of 1:1, and an agitation speed of 250 rpm. Also, shake out tests were conducted for O/A ratio isotherm test and counter-current simulation test. The graphical method for counter-current simulation 4 stage extraction test is in Fig. 3.

The two phases were brought into contact by rapid stirring, and the pH (measured by a Thermo ORION 5 STAR instrument) was controlled by small additions of 5 M NaOH. Although the pH was stable after 2 min, samples were collected in 0.5 pH intervals every 10 min. The collected samples were separated into organic and aqueous types using a separation funnel. To obtain a CMB solution from the loaded organic, stripping was carried out at different HBr con-