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Recovery of high purity cobalt from spent ammonia cracker catalyst

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Abstract

With the ever-increasing demand for cobalt in India it is worthwhile exploiting secondary resources. A step in this direction has been taken in our laboratory at BARC by recovering cobalt from spent ammonia cracker catalyst after leaching with sulfuric acid. The removal of Fe^{3+} and Al^{3+} from the leach liquor can be achieved by either chemical precipitation or solvent extraction using DEHPA as an organic extractant. When nickel is present as an impurity, it is separated by extraction with LIX 84I. This process has been scaled up and it has been possible to obtain a cobalt recovery of ~85% with a purity greater than 99.9%.

Keywords: Ammonia cracker catalyst; Cobalt; DEHPA; LIX 84I; Solvent extraction

1. Introduction

Cobalt has strategic and industrial importance due to its application in many technological fields (Cote, 2000), however, primary sources are presently insufficient to supply demand and secondary sources are being increasingly exploited. Spent ammonia cracker catalyst, from the fertilizer industry, forms an important secondary source of cobalt as it contains ~20% cobalt.

Hence, it was desirable to develop a commercial hydrometallurgical process for the production of cobalt from this source. In this paper the production of high purity cobalt from both nickel-free and nickel-containing catalyst is discussed. The leach liquor obtained in this process is such that the downstream processing can be done using either of the two routes viz. precipitation or solvent extraction. The appropriate route can be chosen depending upon the requirement of purity and throughput as well as the availability of equipment and manpower.

In this process, cobalt and iron were quantitatively leached along with some aluminium. In order to remove iron and aluminium in a single step, it was necessary to convert iron into ferric form. The leach liquor was treated with ammonia for the quantitative removal of Fe^{3+} and Al^{3+}. In an alternate method,

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Fe^{3+} and Al^{3+} were removed by extraction with DEHPA. An additional step of solvent extraction was incorporated, when nickel was also present as an impurity. Cobalt was stabilized in the trivalent oxidation state in ammoniacal medium and nickel was extracted using LIX84I (Cognis, Mining chemicals technology; Website: http://www.cognis-us.com/). Cobalt metal powder was obtained from the pure cobalt solution by the oxalate route.

2. Experimental

The catalyst was obtained from a fertilizer plant in the form of 4–5 mm pellets with the composition in Table 1.

For preliminary laboratory studies the pellets were ground to −250 and −75 μm. Larger scale leaching trials were carried out using 3.0 kg of unground pellets. The catalyst was leached with sulfuric acid at 80 °C for 6 h in a stirred, teflon lined, stainless steel reaction vessel which was heated using a silica coated immersion heater. After leaching, ferrous was oxidised to ferric state with nitric acid at 60 °C for 2 h.

Depending on the type of catalyst, the leach liquor was treated by different routes. Both precipitation and single contact solvent extraction have been adopted for removal of Fe^{3+} and Al^{3+} from the leach liquors of nickel-free as well as nickel-containing catalyst. In the precipitation route, the leach liquor was treated with ammonia to precipitate Fe^{3+} and Al^{3+} as hydroxides at pH 4.0–4.2. In the solvent extraction route, the pH of the leach liquor was adjusted and then contacted with 0.5 M DEHPA giving effective removal of Fe^{3+} and Al^{3+} with minimum loss of Co^{2+}. The Fe^{3+} and Al^{3+} loaded DEHPA was stripped with 6N hydrochloric acid, washed free of the acids, saponified using 50% sodium hydroxide and recycled. A series of experiments were conducted to optimize the feed pH, raffinate pH, contact time, degree of saponification of the solvent and requirement of the solvent to obtain the required purity and recovery of cobalt in the raffinate. Cobalt in the raffinate can be precipitated as oxalate.

Table 1
Typical composition of ammonia cracker catalyst

Constituent	Wt.%
Al_2O_3	36.5
Fe_2O_3	31.5
CoO	29.5
NiO	0.27
K_2O	0.70
Binder	1.53

However, raffinate from the nickel-containing catalyst (Ni:Co 1:100) has to be further treated by solvent extraction for removal of nickel, since nickel coprecipitates with cobalt during oxalate addition thereby reducing the purity. Nickel, and not cobalt, should be extracted to minimise the solvent inventory and make the process cost effective. However, the extractants suitable for sulfate medium (DEHPA, PC-88A and CYANEX-272) all preferentially extract cobalt and hence are not suitable. Selectivity of nickel over cobalt is only possible by oxidising Co(II) to Co(III) and stabilizing it as ammoniacal complex. Ni(II) also forms an ammoniacal complex and does not precipitate at pH 9–11 where it can be extracted using LIX64N or LIX84I. Since LIX64N is no longer available from Henkel Corporation, LIX 84I was used. The raffinate from the first step of solvent extraction, containing cobalt and traces of nickel, was added to 13N ammonia, with stirring followed by calculated quantity of 30% v/v H_2O_2. The process was continued so as to attain a final pH of 10, suitable for extraction of nickel by 10 v/v% LIX84I in kerosene in a single contact giving a purity of >99.9 with respect to Ni. The Ni loaded LIX 84I was stripped with 1 M H_2SO_4 and washed twice with demineralised water before reuse.

The cobalt present as $Co(NH_3)_6^{3+}$ complex in the raffinate is highly stable and cannot be directly converted into cobalt oxalate. Hence, it has to be first converted to cobalt(III) hydroxide by digesting with 50% sodium hydroxide solution at 60–70 °C. The hydroxide was then reductively dissolved in a 1:1 mixture of hydrochloric acid and sulfuric acid. In this reaction, sulfuric acid is used to convert cobalt(III) hydroxide into Co(III) solution, which can then be reduced to Co(II) in the presence of chloride [$E^{\circ}_{redn}(Co^{3+}/Co^{2+})=1.8$ V; $E^{\circ}_{redn}(Cl_2/Cl^-)=1.39$ V]. The reaction occurs as follows:

$$Co^{3+} + Cl^- \Rightarrow Co^{2+} + 1/2\ Cl_2 \quad E_{cell}{}^{\circ} = 0.41\ V$$

The pure cobalt solution obtained from both types of catalyst was converted into cobalt oxalate