Copper, Nickel and Cobalt Extraction from FeCuNiCoMn Alloy Obtained after Pyrometallurgical Processing of Deep Sea Nodules

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ABSTRACT

During pyro-reduction smelting of manganese deep sea nodules from the Clairon Clipperton zone in the Pacific Ocean the copper, nickel and cobalt are concentrated in intermediate product – polymetallic alloy. Characteristic property of the alloy is its high content of iron (65.90%) in compared to copper (12.07%), nickel (12.81%), cobalt (1.33%) and manganese (5.33%). In this paper, a hydrometallurgical scheme for recovery of copper, nickel and cobalt from such an alloy is proposed. The developed scheme includes the following processes: i) selective dissolution of alloy in sulfuric acid in the presence of sulfur dioxide to produce copper-rich (54.9%) sulphide residue and a solution containing iron, nickel, cobalt and manganese; ii) sulphide precipitation of nickel and cobalt from the solution; iii) hydrolysis purification of the solution from iron and manganese; iv) autoclave dissolution of copper and nickel-cobalt sulphide precipitates; v) separation of cobalt from nickel by solvent extraction with Cyanex 272. The obtained electrolytes have a composition suitable for the extraction of copper, nickel and cobalt by electrowinning.

The main advantage of the proposed scheme is the possibility for achievement of a high non-ferrous metals extraction from the alloy and obtaining of copper, nickel and cobalt cathode deposits with standard purity.

KEY WORDS: Hydrometallurgy; manganese nodules; FeCuNiCoMn alloy; sulphuric acid, SO2, autoclave; Solvent extraction, Cyanex 272.

INTRODUCTION

It is known that the development of human civilization is determined by the energy and mineral resources of the earth. Forecasting the market for demand and supply of minerals and metals is a complex task. History has shown the failure of the overly optimistic market forecast in the late 1970s in the terms of consumption levels and prices which effectively delayed full scale commercial deep-sea mining for more than 30 years (Antrim, C, L, 2005). The last two decades however, showed that the increase in metal prices and the rapidly developing economies of China, India, Russia and Brazil reinforce the interest in the resources of the ocean floor (Global Commodity Markets, 2010). Deep sea polymetallic nodules (DPN) represent sedimentary formations that cover the bottom of the oceans and some seas. The largest congregations are registered in Pacific Ocean between Hawaii and California and around Polynesia. According to Metal Bulletin Research (2005) the reserves of metals (Mn, Ni, Cu, Co, Zn etc.) in them are comparable to those of continental ores. A thorough analysis of the operations of DPN in this region is made by LRET Group (B Agrawal, 2012). The authors believe that lack of understanding of many environmental and technological issues associated with their mining from depth 4000-5000 m, is a key parameter in determining the efficiency of processing and high cost of producing basic metals present in nodules.

Currently, a lot of technologies have been developed for the extraction of these metals. They can be divided into two groups: hydrometallurgical and combined pyro-hydrometallurgical. Zhang W. and Cheng C. Y. (2007) have reviewed the various direct reduction processes for the hydrometallurgical treatment of poor manganese ores and polymetallic nodules. They consider leaching with ferrous iron, sulfur dioxide, cuprous copper, hydrogen peroxide, nitrous acid, organic reductants, and bio- and electro-reductions. According to authors among these processes, the leaching with cheap sulfur dioxide or ferrous ion is the most promising. The crucial issue is a purification of leach liquors and selective recovery of copper, nickel and cobalt which is often difficult from solutions containing soluble iron and manganese.

In a combined pyro-hydrometallurgical scheme, manganese enters the manganese slag and nonferrous metals are concentrated in intermediate - polymetallic alloy (Stefanova V. et al., 2009). One characteristic feature of this polymetallic alloy (PA) is its high Fe content (>65%) in comparison with that of Cu and Ni (12-13 %) and especially of Co (0.8-1%). Manganese content in the alloy varies between 5 and 6%. Zequan at al. (1996) proposed a hydrometallurgical scheme for processing of polymetallic alloy based on: i) atomization of the alloy to a particle size <250 µm; ii) dissolution of the alloy in hydrochloric acid in the presence of air or oxygen. At 10% excess of hydrochloric acid a high degree of extraction of these metals in the solution is achieved (98.33% Cu, 97.86% Co, 99.46% Ni and 99.61% Mn). At these conditions over 99% of the Fe is hydrolyzed in the form of ferrous hydroxide. iii) separation of Cu, Ni, Co and Mn ions by solvent extraction using oxime chelating extractant, alkyl phosphoric acid and