

Precipitation of Manganese from Manganese Nodule SO₂-Roast Ammoniacal Ammonium Leach Liquor

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ABSTRACT

Precipitation of manganese from the SO₂-roast leach ammoniacal ammonium sulphate solution bearing both high and low manganese content was carried out in a stainless steel reactor fitted with a turbo grid. Air/O₂ was used to precipitate Mn as MnO₂. There was adsorption loss of cobalt from solution. There was precipitation of 57.2 - 99.96% Mn with loss of 3% Cu, 3.5% Ni and 2.9% Co. The precipitation of Mn and adsorption loss of cobalt from the solution was first order. The rate constants for manganese and cobalt precipitations were evaluated. The data were fitted to Freundlich and Langmuir adsorption isotherms.

KEY WORDS: Manganese nodule; precipitation; manganese; cobalt; kinetics; adsorption.

INTRODUCTION

Ores, concentrates and by-products containing manganese, copper, nickel and cobalt are directly subjected to ammoniacal leaching (Fuerstenaue-Han, 1983; Hubred, 1980) or after pretreatment (Caron, 1950; Siemens-Corrick, 1977). Literature on precipitation of manganese from ammoniacal ammonium sulphate solutions bearing Fe, Mn, Cu, Ni and Co was rare, but such precipitation studies from acidic solutions are available. Precipitation of iron from sulphate solutions of Indian Ocean nodules was carried out at the author's institute by adjusting the pH to 3.5 with lime slurry and heating the solution on a water bath at 85-90°C for one hour. Precipitation of Mn (Nathsarman-Sarma, 1993) from the Fe-free solution with K₂S₂O₈ equivalent to four times its stoichiometric quantity and heating it at 85-90°C for one hour on a water bath lead to quantitative precipitation of Mn with 27% loss of cobalt. Precipitation of manganese as MnO₂ from the zinc electrolyte solution bearing manganese and cobalt (Can. Patent, 1957; US patent, 1978) with K₂S₂O₈ was also carried out in a pilot plant scale in South Africa. Mn(II) was precipitated (Ying-Zhu-Bao-Liu-Wang-Zhang and Youse, 1966) from a chloride solution bearing 11.8 kg/m³ Mn, 105.4 kg/m³ Co, and 0.29 kg/m³ Mg with KMnO₄ at KMnO₄ to Mn mole ratio of 1.12 leading to 99% precipitation of Mn. Precipitation of manganese (Zhang-Singh and Muir, 2002) from an acidic solution bearing Fe, Mn, Co and Ni was carried out with the mixtures of SO₂ and O₂ in the pH range 1-6 and temperature range 25-80°C where oxidation of Mn (II) was first order with respect to SO₂ up to the partial pressure of SO₂ up to 5.7. The rate of Mn oxidation was slow at pH < 3 but increased rapidly at pH > 4.

In the present study, precipitation of Mn from the SO₂-roast leach ammoniacal ammonium sulphate solutions of Indian Ocean manganese nodule bearing Cu, Ni, Co with high and low Mn contents was carried out

in a turbo grid using air/O₂ for 6 hours to arrive at quantitative precipitation of Mn with minimum loss of other metal ions. The experimental data generated in this piece of work are discussed in detail.

EXPERIMENTAL

Powdered Indian Ocean manganese nodule was preheated at 400°C followed by roasting in a Multiple Hearth Furnace within 700-750°C with a mixture of SO₂ and air. The roasted mass was leached in water and filtered. To the filtrate, ammonium sulphate and ammonia were added. Two types of leach liquors with low (6 kg/m³) and high (49 kg/m³) manganese content were separately treated with air/oxygen. The high Mn bearing leach liquor (pH 8.1-9.2) contained 42.75-49.97 kg/m³ Mn, 2.15-2.399 kg/m³ Cu, 2.69-3.525 kg/m³ Ni, 0.553-0.6497 kg/m³ Co, 80 kg/m³ ammonia and 60 kg/m³ (NH₄)₂SO₄ (Table 1). The low Mn bearing leach liquor (pH 9.75-9.9) contained 6.4 kg/m³ Mn, 1.65-1.77 kg/m³ Cu, 1.69-1.98 kg/m³ Ni, 0.26-0.3 kg/m³ Co, 96 kg/m³ ammonia and 200 kg/m³ (NH₄)₂SO₄ (Table 2). The low Mn solution bearing 200 kg/m³ (NH₄)₂SO₄ and 96 kg/m³ ammonia, within the pH range 9.75-9.9, was treated with 3.5 and 5 L O₂/min., and 10 L air/min. The high Mn solution bearing 60 kg/m³ (NH₄)₂SO₄ and 80 kg/m³ ammonia, within the pH range 8.1 - 9.2, was treated with 10 and 30 L/min. of air and 10 L O₂/min. Thirty liters of high Mn solution and forty liters of low Mn solution were separately taken in a 100 L stainless steel reactor fitted with a 2.93 meter long turbo grid (Fig.1). Air from a pump or O₂ from a cylinder at measured flow rates was fed into the reactor while circulating the leach liquor in the turbo grid. The upward moving air/oxygen came in contact with the solution flowing down the turbo grid and escaped out through the vent. Samples collected at intervals of 1 h were filtered through Whatman 42 filter paper, diluted with 1 M HCl and analysed for Mn, Cu, Ni and Co with the Perkin Elmer Model 372 Atomic Absorption Spectrophotometer (AAS).

RESULTS AND DISCUSSION

Powdered and preheated Indian Ocean manganese nodule was roasted with SO₂-air mixture and the roasted mass was digested in water. It was thoroughly mixed and filtered. To the filtrate, ammonium sulphate was added and mixed well followed by the addition of ammonia. The low Mn bearing solutions were buffered more and were more ammoniacal. During preheating of powdered nodule at 400°C, conversion of FeOOH to Fe₂O₃ took place.

