

Leaching of Cobalt-Rich Ferromanganese Crust with Ammoniacal Solutions Using Ammonium Sulfite and Ammonium Thiosulfate as Reducing Agents

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Abstract

Preferential ammoniacal leaching of Co, Ni and Cu from cobalt-rich ferromanganese crust under reducing conditions was performed using ammonium sulfite and/or ammonium thiosulfate as reducing agents. The effects of reducing agent concentration, initial pH, leaching time, temperature and the combined concentration of ammonium sulfite and ammonium thiosulfate on the extraction of Co, Ni, Cu, Mn and Fe were investigated.

The extraction of Co, Ni and Cu with ammonium sulfite was better than that with ammonium thiosulfate. When ammonium sulfite was used as the reducing agent, Mn was precipitated and appeared in the residue as $(\text{NH}_4)_2\text{Mn}(\text{SO}_3)\cdot\text{H}_2\text{O}$.

Key Words: Cobalt-Rich Ferromanganese Crust, Ammoniacal Leaching, Ammonium Sulfite, Ammonium Thiosulfate

1. Introduction

Deep-ocean ferromanganese nodules and cobalt-rich ferromanganese crusts are now widely recognized as potential resources of various metals such as cobalt, nickel and copper. Many nations and groups in the world have been developing mining technology and metallurgical processes for deep-ocean ferromanganese nodules because of their extensive occurrence in the world's oceans. Most of the processing methods developed so far have been based on hydrometallurgical treatment, such as acid leaching (Han and Fuerstenau, 1975; Kanungo and Jena, 1988a, 1988b; Kanungo and Das, 1988) and ammoniacal leaching under reducing conditions (Okuwaki et al., 1974; Okuwaki et al., 1977; Das et al., 1986; Anand et al., 1988; Acharya, 1991).

The cobalt content of cobalt-rich ferromanganese crusts is higher than that of deep-ocean ferromanganese nodules. Therefore cobalt-rich ferromanganese crusts are of particular interest as a source of cobalt. However, studies on the treatment of cobalt-rich ferromanganese crusts are very few (Fujii et al., 1987; Allen et al., 1991; Rokukawa, 1992), because the discovery of the crusts has been relatively recent. Consequently, the properties of cobalt-rich ferromanganese crusts and appropriate processing methods for the recovery of the metals contained have not been established as yet.

This paper presents the result of a study on the preferential ammoniacal leaching of cobalt, nickel and copper from cobalt-rich

ferromanganese crusts under reducing conditions using ammonium sulfite and ammonium thiosulfate as reducing agents.

2. Experimental

2.1. Materials

Cobalt-rich ferromanganese crust sample (Co crust: longitude, 151° 51'E; latitude, 16°44'N) supplied by the Metal Mining Agency of Japan (MMAJ) was air-dried for over a week, then crushed and the base rocks removed by hand sorting. The remaining fragments were ground and sieved to $-74\mu\text{m}$ for the leaching experiments. The chemical analysis of Co crust is given in Table 1.

Table 1 Chemical analysis of cobalt-rich ferromanganese crust

Element	Co	Ni	Cu	Mn	Fe
Content(wt%)	0.59	0.38	0.11	13.1	15.8

The phases in Co crust could not be identified by X-ray diffraction analysis. However, the base rocks associated with Co crust were found from X-ray diffraction analysis to be fluorapatite.

The Hardgrove test, often used as a grindability test of coal, was performed to observe qualitatively the grindability of the crust. Samples used in the Hardgrove test were air-dried Co crust and, Co crust dehydrated at 110 °C for 120 min and base rocks associated with Co crust. The grindability indices obtained from the Hardgrove test (as the value of the Hardgrove grindability index increases, the grindability is better) are given in Table 2 and the Hardgrove grindability indices of various materials (Hardinge, 1960) are given in Table 3 as a reference. Tables 2 and 3 show that the grindability of the Co crust was better than that of coal. In particular, the grindability of the dehydrated sample was good. The grindability of the base rocks was also very good.

2.2. Methods

The leaching experiments were performed in a 1000-cm³ glass reaction vessel equipped with a stirrer, placed in a constant temperature water bath. Requisite amounts of ammonia solution, ammonium sulfate, ammonium sulfite, ammonium thiosulfate and water (total volume 500 cm³) were placed in the reactor with constant agitation at the desired temperature. The total concentration of NH_3 and NH_4^+ was maintained at 2.0 mol/dm³ by adjusting the ammonium sulfate concentration. After