Proceedings of the ISOPE - Ocean Mining Symposium (1995)
Tsukuba, Japan, November 21-22, 1995

ISBN 1-880653-21-4

Carbon Dioxide Fixing-Type Hydrogen Reduction Leaching of Deep-Sea Oxide Minerals Using a Pt/PTFE Catalyst in Ammonium Carbonate Solution at Moderate Temperature and Atmospheric Pressure

T. Konta, T. Ohkoshi, T. Yoshioka and A. Okuwaki
Tohoku University
Sendai, Japan

ABSTRACT

H_2 reduction leaching of cobalt crust was carried out to study the optimum mixing conditions of NH_3-$(NH_4)_2CO_3$-$CuSO_4$ solutions. Cobalt and Ni was extracted 90% or higher in the 2M NH_3-0.5M$(NH_4)_2CO_3$-0.1M$CuSO_4$ solution using a Pt catalyst loaded on polytetra-fluoroethylene (PTFE) under 60°C, 0.5atm of H_2 pressure, 3.3g/l of slurry concentration for 2-3h.

KEY WORDS: cobalt crust, H_2 reduction , hydrophobicity, ammonical leaching, Pt/PTFE catalyst

INTRODUCTION

The deep-sea oxide minerals such as manganese nodules and cobalt crusts are expected as unlimited resources of Co, Ni and Cu in the 21st C, although their contents are low. Though many researches have been carried out including several pilot tests (Okabe and Okuwaki, 1979 a,b) , it is believed that a long lead time would be required for operating the commercial plant. During the long period , it may be possible that the boundary conditions for processing are altered by the global warming due to the CO_2 emission. Although CO (Agarwal et al.,1978) and SO_2 (Rokukawa,1992) reduction processes in NH_3-$(NH_4)_2CO_3$ solution have been developped, one of the most promised processes under such environment is H_2 reduction leaching in NH_3-$(NH_4)_2CO_3$ solutions which has not been studied yet. In such process clean H_2 is used as a reducing agent, and CO_2 emitted in the process can be fixed simultaneously as $MnCO_3$. The problems in H_2 reduction leaching are poor solubility and activity of H_2 at low temperature. On the other hand when H_2 reducton is carried out at high temperature and pressure, each ion of Co, Ni, Cu in the leaching solution might be reduced to the metals. A hydrophobic Pt catalyst loaded on polytetrafluoroethylene (PTFE) membrane filters to activate H_2 gas and a redox couple of Cu(II)-Cu(I) ions are enable to proceed the H_2 reduction leaching under moderate temperature and atmospheric pressure. In the present paper, we report the oputimum conditions for a H_2 reduction leaching of cobalt crust using a Pt/PTFE catalyst in NH_3-$(NH_4)_2CO_3$-$CuSO_4$ solutions.

EXPERIMENTAL

Ore: A cobalt crust sample(AD04) was dredged in north sea area of Samoa of Pacific Ocean. The composition is shown in Table 1. The sample was ground below 200 mesh, washed with water, and dried at 105°C for 2h.

Table I Chemical composition of cobalt crust ADO4/ wt%

Cu	Ni	Co	Mn	Fe
0.22	0.47	0.52	20.63	13.21

Preparation of Pt/PTFE catalyst: A PTFE membrane filter paper, 47 mm in diameter, pore size of 0.2 μm and 0.06 mm in thichness was cut off 8 parts equally, and then cleaned in ultrasonic bath and impregnated for 24h in a 2wt% $H_2PtCl_6 \cdot 6H_2O$ acetone solution. After air-drying the Pt/PTFE catalyst was prepared by H_2 reduction at 200-250 ℃ for 1-2h. The amount of Pt loaded was about 12wt %.

Leaching: A 300ml of 2M NH_3-0.5M $(NH_4)_2CO_3$-0.1M $CuSO_4$ solution was poured in a 500ml 3necked-round bottom flask involving 0.5g of cobalt crusts and Pt/PTFE dipped in a water bath, and a mixed gas of H_2(50%) and N_2 was supplied through a ball-filter after N_2 replacement of the air. Agitation was carried out with a magnetic stirrer. A small portion of the slurry was extracted at certain time interval and filtered. Cobalt and Ni in the filtrate were determined by ICP-AES.

RESULTS AND DISCUSSION

1. Effect of preparation conditions on the activity of Pt/PTFE catalyst

Leaching curves of Co and Ni with Pt/PTFE catalysts prepared under