

## **Treatment of Metal Wastes Containing Ni, Co and Mn with Deep-Sea Manganese Nodules**

**K.H. Park and C.W. Nam**

*Korea Institute of Geoscience & Mineral Resources,  
30 Gajeong-dong, Yuseong-gu, Daejeon, 305-350, Korea*

### **Abstract**

*The spent Ni-Cd battery and the spent catalyst containing cobalt were treated by reduction-smelting process with deep-sea Manganese nodules for recovery of nickel and cobalt metals. The nickel in the spent Ni-Cd battery could be recovered with adding 5% coke as a reducing agent regardless of the amount of battery added. However, to recover cobalt from the spent catalyst, it is required to add more coke for reduction of cobalt oxide in the catalyst. The treatment of metal wastes with manganese nodules can contribute to lower the cost for the processing of nodules and to facilitate the recycling of metal wastes.*

**Keywords:** *Manganese nodules, Reduction-smelting, Spent Ni-Cd battery, Spent catalyst.*

### **INTRODUCTION**

Since their discovery in 19<sup>th</sup> century by the H.M.S. Challenger expedition, manganese nodules has been regarded as an important potential sources of valuable metals including copper, nickel, cobalt and manganese. There are found on the sea-floor throughout the world's oceans in water depths of 4 to 6 km where rates of sediment accumulation are low. In recognition of the economic importance of the manganese nodules, several metallurgical processes have been developed to extract useful metals from this complex resource. There have been well documented in literatures (Black 1981, Agarwal 1979).

Smelting-leaching method is known as one of the most likely processes for the treatment of nodules due to its many advantages on the technical side (best known) and on the economic side (presumably highest return on investment) (Kohga 1995). This process also shows smaller environmental impact: less solid waste as inert slag and easy recovery of manganese. Smelting-leaching process combines classical pyrometallurgical unit operations of the Cu/Ni metallurgy and hydrometallurgical treatments for the final recovery of nickel, copper and cobalt (Sridhar 1976). In addition, manganese is recovered as Si-Mn alloy. In the first stage of reduction smelting in an electric furnace a metal alloy and a slag containing the manganese is obtained. This slag represents the feed of the Si-Mn alloy production. The metal alloy is charged to a converter, where matte is formed by addition of sulphur bearing materials. The matte basically contains copper, nickel cobalt, and iron. The slag obtained containing almost all the iron is recycled to the first stage of smelting. The matte is granulated, slurried, and pressure leached with sulphuric acid at elevated temperature. The unit operations for the final recovery of valuable metals are precipitation solvent extraction and electrowinning. Figure 1 shows the brief flow sheet of smelting-leaching process.

In smelting process, there are not strict restrictions on the composition and properties of the feed ore or materials compared with hydrometallurgical one. This work studied the treatment of the spent Ni-Cd battery and the spent catalyst containing cobalt with reduction smelting process of manganese nodule. The effects of the ratio of nodules to the spent materials and the amount of reducing agent added were mainly investigated.

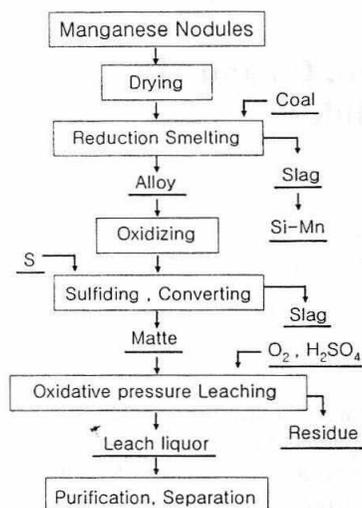


Table 1: Chemical Composition of Samples used in This Test (Wt%)

Element	Fe	Cu	Ni	Co	Mn
Manganese Nodules	8.85	0.73	0.97	0.18	22.35
Spent Ni-Cd battery	0.45	-	79.78	2.26	0.06
Spent catalyst	5.17	0.06	0.13	18.79	28.61

Fig. 1. Smelting-leaching process of Mn Nodules

## EXPERIMENTAL PROCEDURES

### Sample

Manganese nodule sample was collected from the Pacific Ocean (Clarion-Clipperton Fracture Zone) were crushed and ground to minus 70 mesh in ball mill. This sample was dried at 110°C for 24 hours. The spent Ni-Cd battery was prepared from the residue in which cadmium was removed by vacuum distillation. This residue mainly consisted of nickel, iron and a small amount of cobalt. This was crushed by a hammer crusher and then screened to -20 mesh size. Cobalt manganese bromide catalyst was used after oxidation roasting to remove bromide. Table 1 shows the chemical compositions of the samples used in this work.

### Experimental Apparatus

Vertical tube furnace (ID 60mm) heated by silicon carbide elements was used for reduction smelting of samples (Fig. 2). Electronic balance was used to monitor the sample weight during experimentation. The crucibles used were made up dense and fine grained alumina. R type (Pt-13Rh/Pt) thermocouple was inserted inside the tube to monitor and control the temperature.

### Procedures

Manganese nodules was heated at 900°C for 2 hours to remove the bounded water and mixed with the spent Ni-Cd battery or the spent catalyst. The total weight of these samples was 100 grams. A certain amount of coke as a reducing agent and 10g SiO<sub>2</sub> and 10g CaO as fluxes were added to the samples and mixed. The mixed materials were placed in the crucible. The water-cooled end cap was secured to the furnace and the entire assembly was purged with nitrogen gas with flow rate of 5 ml/min. The temperature of furnace increased to 900°C with 10°C/min and held for 1 hour for preliminary reduction. After then, the temperature increased to 1450°C with 5°C/min and held for 1 hour for smelting (Nam 2003). After room cooling, the alloy and slag phases were separated and weighted. Chemical analysis was then performed for all the metals of interest to determine their recoveries to alloy phase.

## RESULTS AND DISCUSSION

### Spent Ni-Cd Battery

Figure 3 displays the thermodynamic stabilities of the oxides manganese, nickel, copper, cobalt and iron. It shows that it is possible to reduce the solid oxides of nickel, copper, cobalt and iron to metal forms while leaving the manganese oxide over the wide ranges of temperature with controlling the amount of reducing agent added.

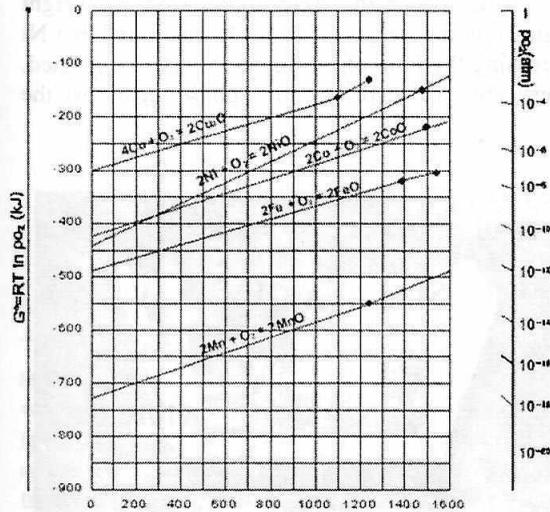


Fig. 2: Standard free energies of formation of metal oxides

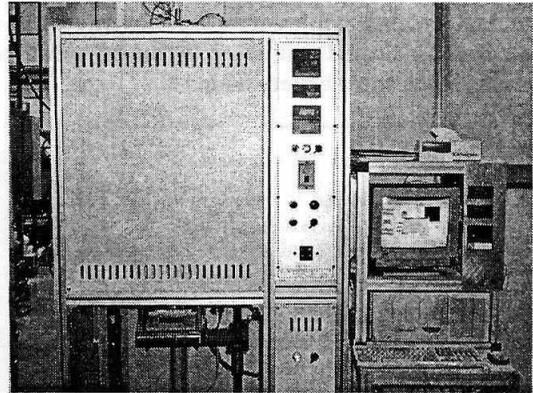


Fig. 3: Vertical Type Tube Furnace used in this Study

Effect of amount of coke as a reducing agent on the recovery of nickel to alloy phase was investigated with 95g manganese nodules and 5g spent Ni-Cd battery. Fig 4 shows that the recovery of nickel increased with increasing the amount of coke added from 3g to 5g. 88.8% of nickel recovered with 3g coke and as compared to 100% recovery with 5g coke. This result is similar to that of pure manganese nodules and this is due to the reason that nickel in the spent Ni-Cd battery is metal form (Park 1999) and it does not necessary to add any reducing agent.

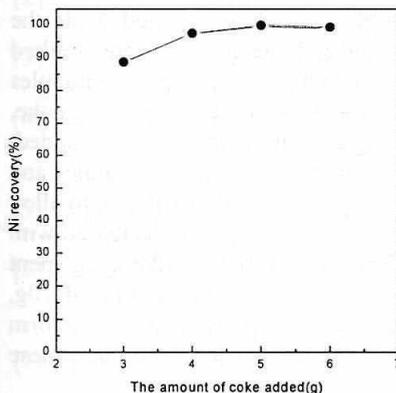


Fig. 4: Effect of Amount of Coke Added on Recovery of Nickel in Alloy Phase

Table 2: Effect of Amount of Coke on Metal Weight in Alloy (Mn Nodules 95g, Spent Ni-Cd Battery 5g)

Coke (g)	Metal weight in alloy (g)					Total
	Cu	Ni	Co	Fe	Mn	
3	0.702	4.360	0.119	0.396	0.002	5.579
4	0.778	4.744	0.229	3.341	0.047	9.145
5	0.812	4.790	0.296	5.212	0.289	11.399
6	0.822	4.788	0.292	5.182	0.423	11.507

Table 2 shows metal weight in alloy with various amounts of coke as a reducing agent. The amount of coke in these experiments was varied in the range of 3 – 6 g/100g sample. As shown in the table, the recoveries of metals (Cu, Ni, Co and Fe) increased with increase of coke addition up to 5 g. At this addition, most of the metals were extracted to the alloy phase. However, manganese was remained in slag up to the addition of 5 g coke. After addition of 5g more coke, manganese started to transfer to alloy phase. Therefore the optimum weight of coke is fixed at 5g for reduction smelting.

Fig 5 shows the effect of ratio of the spent Ni-Co battery to manganese nodules on Ni weight recovered with adding 5 g coke and the ratio was changed in the range 0 – 20%. It was found that Ni and total weights of alloy increased linearly with increasing the ratio of the spent battery as expected. This result indicated that all nickel in the spent battery was extracted into alloy phase regardless the amount of the spent battery added.

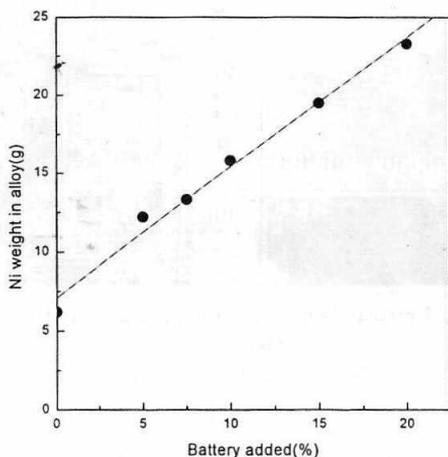


Fig. 5: Effect of Amount of Spent Ni-Co Battery Added on Ni Weights in Alloy

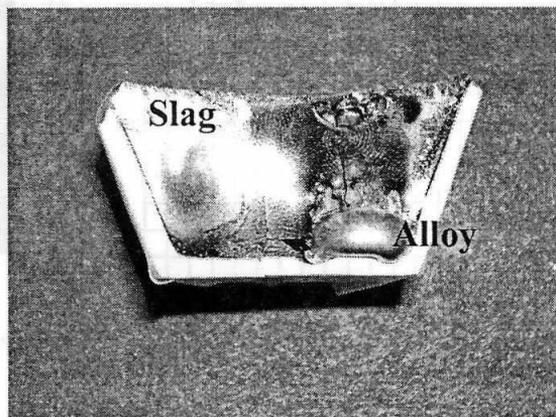


Fig. 6: Alloy and Slag Produced by Smelting

Fig 6 shows the alloy and slag phases produced by smelting of 95g manganese nodules and 5g spent Ni-Cd battery with adding 5 g coke as a reducing agent, 10g SiO<sub>2</sub> and 10g CaO as a flux.

### Spent Catalyst

In the experiments, the distribution of metals of interest to alloy phase was investigated while the mixtures of manganese nodules and spent catalyst containing cobalt and manganese were smelted with reduction condition. Fig 7 shows the effect of the ratio of spent catalyst to manganese nodules on weight of alloy produced. This ratio was varied in the range of 0 – 20% with adding of 5 g coke, 10g SiO<sub>2</sub> and 10g CaO. The weight of alloy increased with increasing amount of spent catalyst added. The recoveries of cobalt, nickel, copper, iron and manganese into alloy from manganese nodules and spent catalyst was also investigated as shown in Fig 8. All copper and nickel were distributed to alloy phases regardless the amount of spent catalyst added. However, the recovery of cobalt decreased with increasing the amount of spent catalyst. For example, 100% cobalt was recovered by adding 5g spent catalyst, but the recovery decreased to 97.4%, 92.9% and 82.3% respectively with addition of 10g, 15g and 20g of spent catalyst. It is due to the reason that cobalt in spent catalyst is cobalt oxide form (Park 2001) and more coke is required to reduce it as cobalt metal. On the other hand, all manganese in spent catalyst was distributed to slag phase.

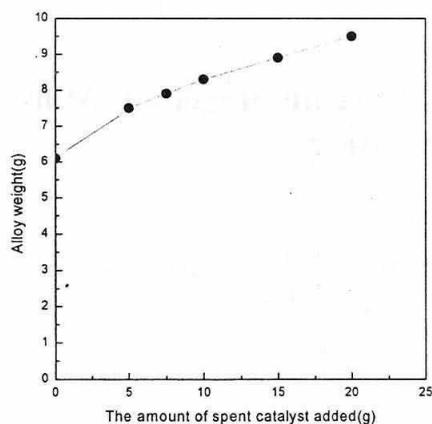


Fig. 7: Effect of Amount of Spent Catalyst Added on the Alloy Weight

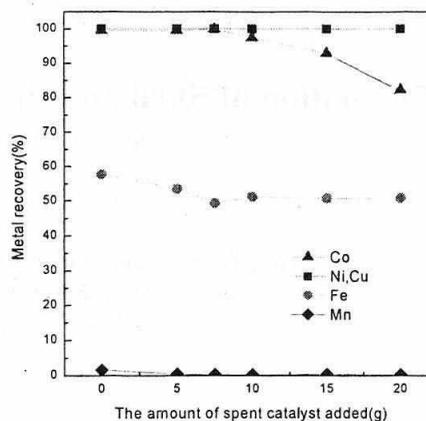


Fig. 8: Effect of Amount of Spent Catalyst Added on Metal Recovery

## CONCLUSIONS

The spent Ni-Cd battery and CMB catalyst were treated with manganese nodules with reduction smelting process to recover valuable metals. All nickel in manganese nodules and spent Ni-Cd battery was recovered to alloy phase by adding 5% coke as a reducing agent and flux regardless the ratio of spent catalyst to manganese. For cobalt recovery from the spent catalyst, more coke is required for reduction of cobalt oxide in the catalyst. Manganese in catalyst was distributed to slag phase. The treatment of metal wastes with manganese nodules can play a role to cut down the cost for the processing of nodules and to facilitate the recycling of metal wastes.

## ACKNOWLEDGEMENT

The authors are grateful to Ministry of Maritime affairs and Fishers, Korea government for sponsoring the project.

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