

Development of Manganese Recovery Process from Waste Dry-Cell Batteries

YAMAGUCHI Toyoshi^{*1} SUGIMORI Hiroichi^{*2}

Abstract:

High purity manganese is necessary for high strength steel production. Metal manganese is available from limited countries. Therefore, production of an alternative to metal manganese was investigated. Waste dry-cell batteries are considered to be one of the most feasible manganese sources. JFE has developed a high efficiency chemical separation system. This system consists of three-phase chemical treatment. In the first phase, metal components of the waste dry-cell batteries were dissolved by acid and reducing agent. Next, undissolved carbon particles were separated by filtration. In the second phase, dissolved manganese was selectively precipitated as manganese oxide by ozone oxidation. Then, manganese oxides were separated from other metal components by filtration. In the third phase, the manganese oxide was reduced by an electric arc furnace. After these treatments, high purity manganese was produced from waste dry-cell batteries.

1. Introduction

Due to depletion of metal resources and increased metal prices, recovery of valuable metals from low-grade ores, steel works byproducts and industrial wastes has become an important issue in recent years.

Manganese (Mn) is an essential material for the production of high strength steel¹⁻⁴⁾. Because high strength, high ductility steel contributes to improved automobile safety and fuel efficiency through vehicle weight reduction, demand for this type of steel has increased⁵⁾. A number of studies have investigated the production of high strength steel, and at the same time, the microstructure of these steels has also been evaluated by electron microscope analysis⁶⁻⁸⁾.

However, the possibility that demand for manganese will exceed the estimated reserves is a particular concern. In recent years, Japan has imported approxi-

mately 80 kt/y of metallic Mn, most of which is used in the steel industry.⁹⁾ Since metallic Mn is added in the last phase of the steelmaking process to adjust the quality of the steel, a stable supply of high quality manganese is needed.

Securing manganese resources is crucial in the steel industry. In particular, since the countries from which metallic Mn can be imported are limited⁹⁾, there are various risks in terms of resource security.

On the one hand, some types of dry-cell batteries contain large quantities of manganese¹⁰⁾. Manganese dioxide is used as a positive electrode material in manganese dry cells and alkaline manganese dry cells. In recent years, alkaline manganese dry-cells have been produced in large quantities. The manganese contents of manganese dry-cells and alkaline manganese dry-cells are about 9–14% and 16–20% respectively¹⁰⁾. The major components other than manganese are zinc, carbon and iron. In Japan, these dry-cell batteries are produced and consumed in large numbers¹¹⁾, but only a small amount of their zinc, iron, and carbon contents has been recycled, and manganese has been hardly recycled as a metallic resource due to the difficulty of separating manganese from other components.

Therefore, a process for producing manganese from waste dry-cell batteries was investigated, focusing on the production of an alternative to virgin metallic Mn.

2. Materials and Methods

First, waste Mn dry-cells and alkaline Mn dry-cells were crushed, screened (<2.8 mm), and magnetically separated. As a result, powder and granular materials were obtained. The chemical composition of these materials is shown in **Table 1**. In conducting this study, it was necessary to separate Mn from Zn, C and Fe.

[†] Originally published in *JFE GIHO* No. 53 (Feb. 2024), p. 12–17

^{*1} Dr. Eng., Senior Researcher Deputy General Manager, Sustainable Materials Research Dept., Steel Res. Lab., JFE Steel

^{*2} General Manager, Research Planning & Administration Dept., Chrome & Recycle Division, JFE Mineral

Table 1 Chemical composition of powder and granular materials of waste dry-cell batteries

(Mass%)						
Mn	Zn	C	Fe	Cr	Cu	Ni
33.1	24.3	7.1	0.34	<0.003	0.003	0.21
Pb	Cd	P	S	K	Cl	
0.02	0.002	0.003	0.3	4.58	2.47	

2.1 Mn Leaching by H₂SO₄ and Selection of Reducing Agent

First, an acid leaching test of the powder and granular materials was conducted using only H₂SO₄. The solid-liquid ratio was 1: 10, and the concentration of H₂SO₄ was varied. The treatment time was 1 h. After this acid leaching test, solid-liquid separation was conducted. The Mn leaching ratio was evaluated by determining the concentration of Mn in the solid and liquid phases.

Next, the effects of various reducing agents on Mn leaching were evaluated. As reducing agents, H₂O₂, Na₂S, NaHSO₃, Na₂S₂O₃ and FeSO₄ were added to the H₂SO₄ solution and tested.

2.2 Mn Recovery by O₃ Oxidation

Mn recovery was then carried out by O₃ treatment of the leachate¹²⁾. The experimental apparatus is shown in Fig. 1. A 1.2 L bubble-column reactor was used. The filtrated leachate was ozonated under a strongly acidic condition, and only Mn was precipitated as MnO₂.

The methods selected for the evaluation of the O₃ reaction rate were use of gas detector tubes and titration of a KI solution. The gas detector tube method was able to detect the gas concentration in a short time and track the O₃ reaction rate in real time. The O₃ reaction rate was calculated from the difference between the input and output gas concentrations. On the other hand, it was possible to evaluate the overall reaction rate by titration of the KI solution.

2.3 Reduction of Mn by Electric Furnace

The recovered MnO₂ was reduced using an electric furnace. This electric furnace was a 50 kVA test furnace with a capacity of 100 kg. A reduction method using an electric furnace with Al thermite was selected based on the method used in ferroalloy production. Al was used as the metal reductant, and lime was used as the flux.

The recovered MnO₂ (50 kg) and other raw materials (Al + CaO) were charged and melted in the electric furnace.

The detailed operating method of the electric furnace is shown in Fig. 2. First, part of the raw materials

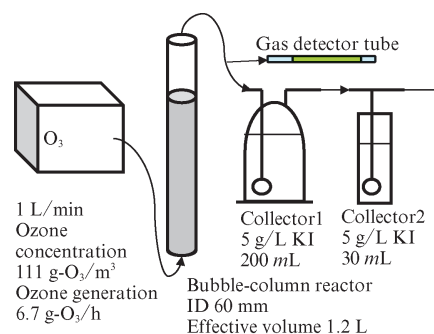


Fig. 1 Experimental apparatus for ozone oxidation

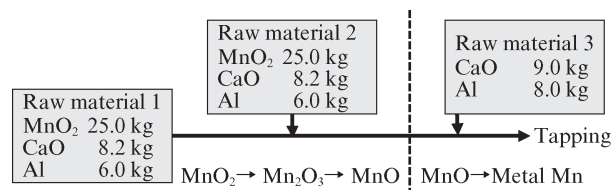


Fig. 2 Operating method of the electric arc furnace

was charged and the electrodes were lowered into the electric furnace. Then, an electric current was applied and the raw materials were melted. When the Al thermite reaction occurred, the electricity was cut off to avoid overheating. After repeating this operation, the oxidation degree was decreased from MnO₂ to MnO. This MnO was finally reduced to metallic Mn by a finishing reduction process.

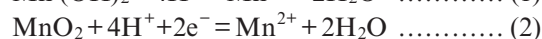
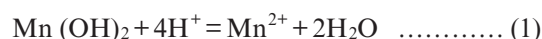
Since C has a higher affinity for metal than for slag, the electrodes used in the furnace were protected from contact with the molten metal in order to reduce C contamination.

Refining of Mn was also conducted in this process, and the quality of the reduced Mn was evaluated by detailed analyses.

3. Results and Discussion

3.1 Mn Leaching by H₂SO₄ and Selection of Reducing Agent

The results of the acid leaching test of the powder and granular materials using only H₂SO₄ are shown in Fig. 3. The Mn leaching rate was no more than 30%, and the effect of increasing the H₂SO₄ concentration on the Mn leaching rate was small. On the other hand, most of the Zn was leached. The chemical forms and leaching reactions of Mn in the powder and granular materials are given by the following equations:



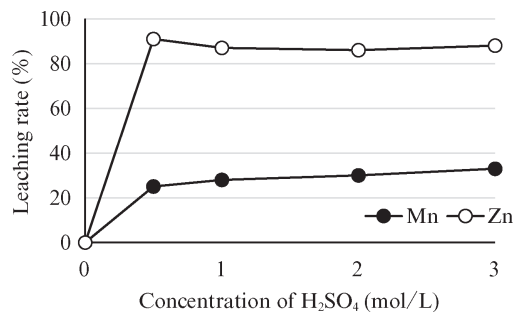


Fig. 3 Leaching results by only sulfuric acid

As shown in Eqs. (2) and (3), electrons from the reducing agent are needed in order to leach MnO_2 (tetravalent) and MnOOH (trivalent). Most of the Mn in waste dry-cells is in the form of MnO_2 and MnOOH . In order to leach these forms of Mn as divalent ions, a reducing agent was necessary. Therefore, the leaching efficiencies of several reducing agents were evaluated.

Figure 4 shows the effect of the various reducing agents on the Mn leaching rate. Mn was completely leached when H_2O_2 , Na_2S or NaHSO_3 was used, and almost all Zn was also leached by treatment with these reducing agents. Hydrogen peroxide was selected and used as the reducing agent for the subsequent experiments due to its easy handling and low cost.

3.2 Mn Recovery by O_3 Oxidation

The potential-pH diagrams of Mn, Zn and Fe are given in **Fig. 5**¹³⁾. These diagrams were generated by PHREEQC^{14,15)} and PhreePlot¹⁶⁾. The equilibrium temperature was set at 25°C, and the concentration of each of the elements was set at 0.5 mol/L.

A mechanism for the separation of Mn as MnO_2 from the other elements was formulated using these diagrams. Metals are usually leached under an acidic condition. However, only Mn is precipitated as MnO_2 under a strong acidic and high oxidative condition. O_3 oxidation was adopted to achieve such a high oxidative condition.

The filtrated leachate became turbid immediately upon ozonation, and the generation of solids was confirmed.

Table 2 shows the results of the elemental analyses of the recovered solids. The Mn content of this sample was 55.5%, which corresponds to 88% of the MnO_2 in the recovered products detected by X-ray diffraction analysis. Except for the crystallization water, most of the solids were MnO_2 . Thus, recovery of high-purity Mn was confirmed. Mn was almost completely recovered, and was separated from Zn in the leachate. During ozonation, some Fe was precipitated with Mn. However, the Fe content of the raw materials was low,

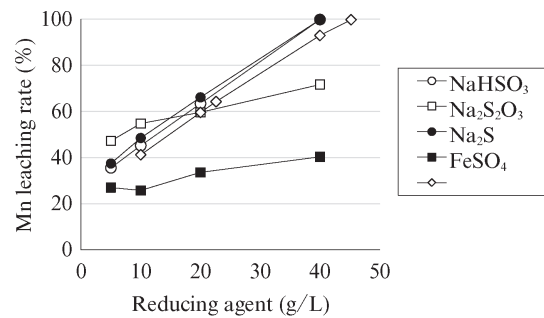
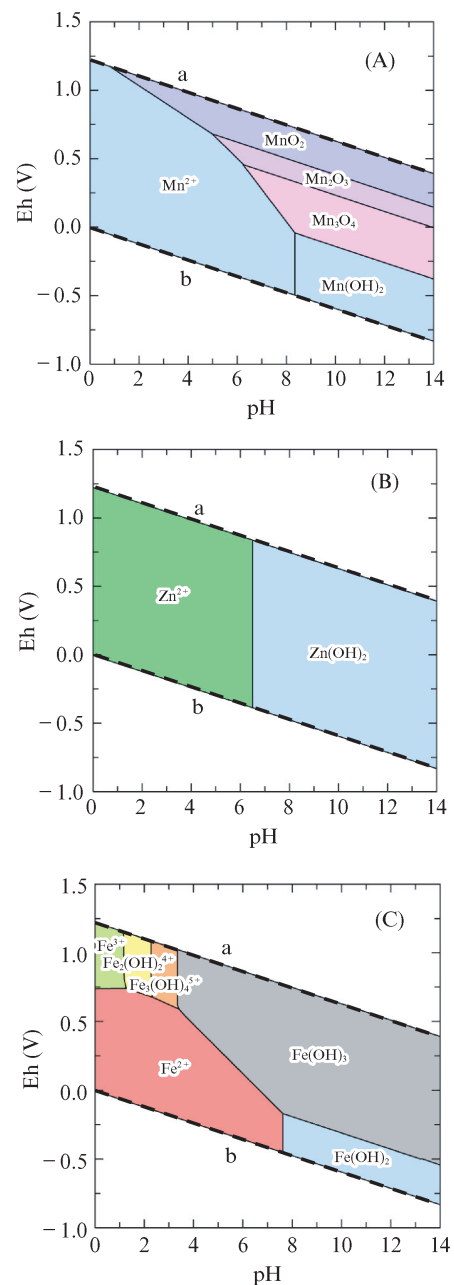
Fig. 4 Effect of reducing agents on the Mn leaching rate (H_2SO_4 : 1 mol/L)

Fig. 5 Potential-pH diagrams of manganese (A), zinc (B) and iron (C) at 25°C: a, b = lines describing the thermodynamic zone of water stability

Table 2 Chemical composition and yield of recovered MnO₂

	Mn	Zn	Fe	C	P	S	Moisture
Content (mass%)	55.5	0.69	0.15	0.01	0.004	0.8	10
Yield (%)	99.9	0.1	32.2	—	—	—	—

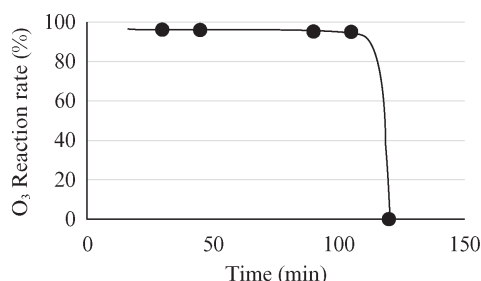


Fig. 6 Time course of the ozone reaction rate

so Fe contamination was on an acceptable level.

As a result, highly efficient separation of Mn was achieved by using the acid leaching and ozonation processes.

Figure 6 shows the time course of the O₃ reaction rate obtained by the gas detector tube method. The reaction was finished at about 120 min, and the reaction rate was maintained at a high efficiency. An earlier study reported that the MnO₂ generating reaction by O₃ was a zero-order reaction¹²⁾. Therefore, it was presumable that the reaction rate did not decrease in the latter half of the reaction.

After the ozonation reaction, KI solution titration was conducted. The overall O₃ reaction rate was determined to be 95.8%. Most of the O₃ was utilized for Mn oxidation. Consequently, a high O₃ reaction rate was confirmed from these results.

Bulk production of MnO₂ was also attempted. In this test, production of 500 kg of MnO₂ was outsourced to a contract manufacturer. In order to reduce the reactor volume, the solid-liquid ratio was changed from 1:10 to 3:10, and the concentrations of H₂SO₄ and H₂O₂ were increased threefold. As a result, 500 kg of MnO₂ was produced successfully. The results of the elemental analysis of this MnO₂ were almost identical to those of the laboratory-scale experiments.

3.3 Reduction of Mn by Electric Furnace

First, the type of reduction process to be applied was considered, as shown in **Fig. 7**. Three kinds of reduction processes were selected as candidates.

The first method was simple reduction of Mn by Si. However, this method was predicted to increase the C content while decreasing the Si content.

The second method was production of Si-Mn in a

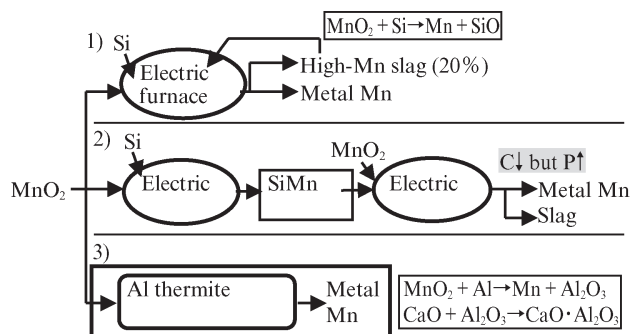


Fig. 7 Estimation and selection of the reduction process

Photo 1 Reduction of MnO₂ by electric arc furnace

pretreatment step. This method can lower the C content, but an increase in the phosphorus content from lime was predicted. In addition, the cost of this treatment tends to be high.

The third method was a combination of an Al thermite reaction and use of an electric furnace. This method was considered to solve all the problems of the first two methods mentioned above. Based on this estimation, the third method was chosen for the present study, and reduction of MnO₂ using an electric furnace with the Al thermite reaction method was performed.

In order to reduce the C contamination by the electrodes, the electrodes were protected from contact with the molten metal. First, the oxidation degree was decreased from MnO₂ to MnO. Then, MnO was reduced to Mn by a finishing reduction reaction process. **Photo 1** shows the actual reduction of MnO₂ by the electric arc furnace. The reaction was conducted using a test electric furnace (500 kVA). Al (metal reductant) and CaO (metal refining flux) were charged into the furnace with the recovered MnO₂.

Table 3 shows the quality of the products. Each resulting product meets the target. In this experiment, C from the electrodes slightly contaminated the metal. However, in a full-scale electric furnace, the C content

Table 3 Quality of conventional Mn products and our product

	Mn	C	P	S	Si	Al
Electrolytic metal Mn	99.7 min	0.04 max	0.005 max	0.05 max	—	—
Low C, P Fe-Mn (Alternative to metal Mn)	90 min	0.1-0.2 max	0.05 max	0.02 max	1.2 max	—
Target values in this study	95 min	0.2 max	0.02 max	0.05 max	0.3 max	—
This study	95.9	0.1	0.01	0.03	0.2	2.2

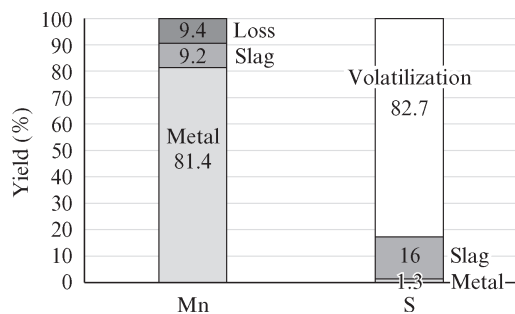


Fig. 8 Yield of manganese and sulfur in the reduction process

is expected to decrease (0.07–0.08%) due to the difference in the scale of the furnace volume and the contact area of the electrodes. In a steelmaking process, metal Mn is added in the last phase of the steelmaking operation for steel quality adjustment. In this phase, Al is added simultaneously as a deoxidant, so some Al contamination of the Mn product is acceptable as long as the Al concentration is stable.

The yield of Mn and S is shown in **Fig. 8**. The Mn yield as metallic Mn was 81%, while some Mn was discharged with the slag or counted as loss. On the other hand, most of the S was volatilized, and S contamination of the metal was very low (Table 3).

Figure 9 shows the relationship between the yields of Al and Mn. The Mn yield (a) and the Mn in the slag (b) did not change drastically after exceeding a certain reducing equivalent. It is possible to stably adjust Al in the metal by analyzing the relationship between the Al in the metal and the Mn in the slag. The optimum operating condition was considered to occur at an Al reducing equivalent of 110.

The material and heat balances of the electric furnace reduction process are shown in **Fig. 10**. When using the combination of the Al thermite reaction and the electric furnace, 470 kg of metallic Mn and 670 kg of slag were generated from 1 ton of MnO_2 .

In terms of the heat requirement, the heat of the Al thermite reaction was utilized, and the balance of the

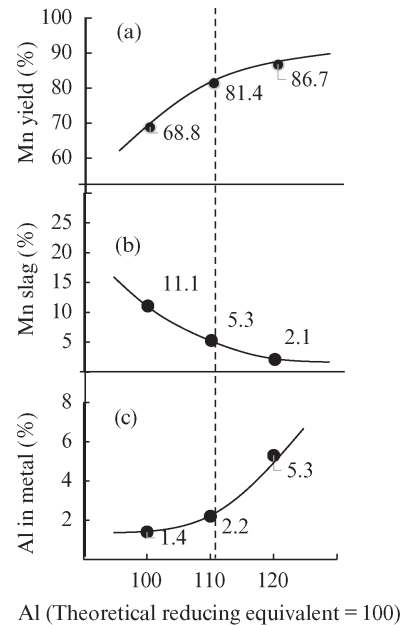


Fig. 9 Relationship between aluminum and manganese yield

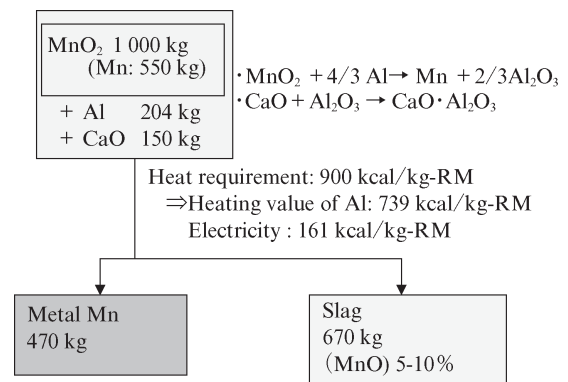


Fig. 10 Material and heat balance of reduction by electric arc furnace

heat needed was compensated by electricity.

Figure 11 shows the overall and detailed material balance of the method used in the present study. About 300 kg of metal Mn was produced from 1 ton of powder and granular materials obtained from waste dry-cell batteries. The residue contained a large quantity of C. The higher heating value (HHV) of this residue was about 18.3 MJ/kg, which corresponds to the HHV of woody biomass^{17–19}. Thus, the residue has the potential to be used as fuel. High-purity (69%) Zn sludge was obtained after treatment of the residual liquid by alkaline precipitation. Therefore, this sludge can be recycled as a Zn source.

It is assumed that these byproducts from the metallic Mn production process can be utilized as valuable materials.

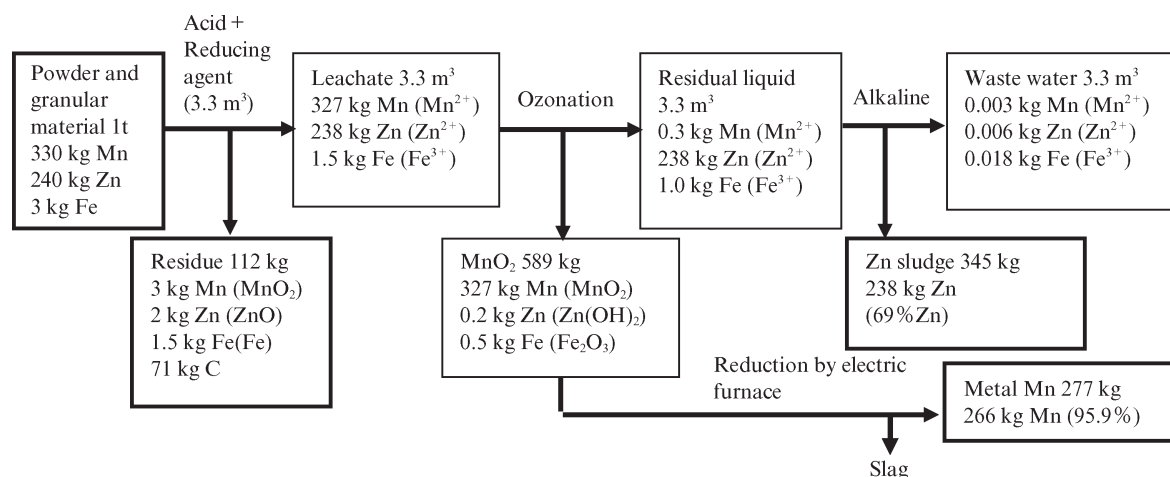


Fig. 11 Overall and detailed material balance of proposed process

4. Conclusion

From the results of this study, high-quality metallic Mn could be produced by the proposed process. A high efficiency chemical separation system that could separate Mn from waste dry-cell batteries and produce high-purity metallic Mn was developed.

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