RETRACTION

The following article was withdrawn by the Editorial Board of ISIJ International on October 31, 2014, because it was submitted without consent of the coauthors.

Retraction: Gaseous Pre-reduction for the Magnetic Beneficiation of Ferruginous Low-grade Mn Ore

Yubo GAO,¹⁾ Hang Goo KIM,¹⁾ Hong Yong SOHN¹⁾ and Chan Wook KIM²⁾

1) Department of Metallurgical Engineering, University of Utah, Salt Lake City, Utah, 84112 USA.

2) Research Institute of Industrial Science and Technology, Pohang, Korea.

This article was published in *ISIJ Int.*, **52** (2012), No. 5, 759–763.

Gaseous Pre-reduction for the Magnetic Beneficiation of Ferruginous Low-grade Mn Ore

Yubo GAO,¹⁾ Hang Goo KIM,¹⁾ Hong Yong SOHN¹⁾ and Chan Wook KIM²⁾

1) Department of Metallurgical Engineering, University of Utah, Salt Lake City, Utah, 84112 USA.

2) Research Institute of Industrial Science and Technology, Pohang, Korea.

(Received on July 19, 2011; accepted on December 5, 2011)

Because of intensive mining of high-grade manganese ores for a long time while leaving behind the low-grade ores, the utilization of the latter has become necessary. In this study, ferruginous low-grade manganese ore was selectively reduced by CO, which converted iron oxide to Fe_3O_4 while manganese oxide was reduced to MnO. The iron-rich component was then separated by magnetic separation. The effects of sample particle size and various reduction parameters on the efficiency of magnetic separation were studied. Under the optimum experimental conditions, the manganese content in the ore increased from around 36% to more than 44%, and almost 50% of iron was removed at a Mn loss of around 5%.

KEY WORDS: manganese ore; upgrading; selective reduction; magnetic separation; ferromanganese; manganese mineral.

1. Introduction

Manganese is an element of considerable importance for the steelmaking industry. During the steelmaking process, it is added as a desulfurizer, a deoxidizer or an alloy additive in such forms as ferromanganese, silicomanganese and manganese metal, all of which are produced from manganese ores. Manganese ores are classified by their Mn contents, as shown in **Table 1**.¹⁾

The intensive mining of high-grade manganese ores has brought about the unavoidable problem of utilizing the low-grade ores. There are several physicochemical differences among the components in manganese ores, which can be used for the enrichment of manganese. In particular, for the abundant manganese ores containing iron oxide, it is not thermodynamically possible to reduce manganese oxides to go beyond MnO by C or CO at temperatures from 400 to 1 000°C, while the iron oxide can be reduced to Fe_3O_4 or metallic Fe. The latter two are strongly magnetic, while the manganese oxides are weakly magnetic or non-magnetic. Therefore, the ferruginous low-grade manganese ore may be upgraded by selective reduction and magnetic separation.

For the upgrading of ferruginous low-grade manganese ore by magnetic separation, several studies^{2–4)} on selective reduction using solid carbon have been reported. In comparison with solid carbon, reduction by CO may result in a faster rate even at a lower temperature, owing to the advantages of gaseous reduction over carbothermal reduction.⁵⁾ Up to

now, little research has been carried out on the gaseous reduction of manganese ore by CO, and a further study on selective reduction by CO is essential to develop effective and suitable techniques for the beneficiation of ferruginous low-grade manganese ores.

In addition to manganese enrichment, such a study can also lead to other potential benefits such as savings in coal and power consumption in the subsequent smelting process for the production of manganese alloy as well as utilization of the off-gas from the smelting furnace itself.

2. Experimental

2.1. Materials

The chemical composition and XRD pattern of manganese ore used in this study are given in **Table 2** and **Fig. 1**, respectively. It is of low manganese content (36.6%) and low Mn/Fe ratio (2.8). For the production of ferromanganese alloy, it was reported by Kothari and Nilkantha³⁾ the Mn/Fe ratio in manganese ore should be at least 5:1. As shown in Fig. 1, the manganese in this ore is mainly in the form of MnO_2 , and trace of manganese is present as $\text{KMn}_8\text{O}_{16}$. The iron exists as Fe_2O_3 and $\text{FeO}(\text{OH})$.

2.2. Apparatus

The reduction experiments were carried out by using a horizontal resistance furnace with a stainless steel tube

Table 1. Classification of manganese ores.

Grade	High Grade	Medium Grade	Low Grade	Steel Mill Grade
% Mn	> 44	40–44	35–40	28–35

Table 2. Chemical composition of “LP” manganese ore.

Chemical Composition						
T–Mn	T–Fe	SiO_2	Al_2O_3	CaO	P_2O_5	MgO
36.6	12.7	11.7	4.01	0.12	0.17	0.11

Fig. 1. XRD pattern of "LP" manganese ore.

Fig. 2. Schematic diagram of experimental apparatus.

(inside diameter: 40 mm, outside diameter: 55 mm, length: 1 200 mm). The temperature of the furnace was controlled by a Lindberg temperature controller (model: 59545, series No.:800067), and the temperature of sample was measured by a K-type thermocouple. The schematic diagram of experimental apparatus is given in Fig. 2.

2.3. Procedures

The original manganese ore, designated "LP", used in this study were milled and sieved. The most frequently used size of sample particles was less than 105 μm . However, several different size fractions were also prepared so that the effect of particle size on the magnetic separation could be investigated. In each test, the sample weight was around 30 g.

Prior to reduction experiments, the milled sample particles were calcined at 900°C for 3 hours in Ar, so as to remove the volatile component and to decompose the hydrates and carbonates contained in the ore. In this study, the selective reduction of low-grade manganese ore was conducted by using a gas mixture of CO and CO₂ as the reducing agent in the temperature range of 400–700°C. The total gas flow rate was maintained at 1.5 NL/min. While manganese oxide was converted to MnO, which is non-magnetic, iron oxide was reduced only to Fe₃O₄, because of its stronger magnetism and lower requirements in power and reduction gas consumption compared with reducing it to metallic Fe. The selectivity of reduction was achieved by controlling the reduction conditions at the overlapped stable region of MnO and Fe₃O₄ in the corresponding equilibrium

Fig. 3. Temperature-oxygen potential diagram for the Mn-Fe-O system.

diagram, as shown in Fig. 3.

The reduced particles were reground, followed by magnetic separation with a magnet whose magnetic strength was 870 Gauss. The Mn and Fe contents of various reduced and separated samples were analyzed by inductively coupled plasma (ICP).

A preliminary test was first undertaken to study the feasibility of magnetic separation for selectively reduced sample particles. In the subsequent single-factor experiments, the effects of particle size and such other parameters as reduction time, temperature, and CO content were determined. Based on the test results of these single-factor experiments, a two-level full factorial design was further used to investigate the significance and interactive effects of different reduction parameters.

3. Results and Discussion

3.1. Preliminary Test

In the preliminary test, sample particles were reduced at 600°C for 5 hours, using a mixture gas of CO and CO₂ (CO/CO₂ = 30/70, Log (P_{O_2} / P^0) = -23.99). The particles used in this test were in the size range of 500–1 000 μm .

The XRD patterns of magnetic and non-magnetic parts are shown in Figs. 4 and 5, respectively. It is seen that, while the magnetic part mainly consists of Fe₃O₄ and MnO, the major phases contained in the non-magnetic part are MnO, SiO₂, and Al₂O₃. Therefore, iron was effectively concentrated to the magnetic part. A certain amount of MnO was also detected in the magnetic part, although it is not magnetic.

3.2. The Effect of Particle Size

To investigate the effect of particle size on the efficiency of magnetic separation, experiments were carried out with samples screened to various size fractions under the same conditions as described above. The results were evaluated in terms of the following factors:

$$\% \text{ Fe removed} = \frac{\text{Amount of Fe in magnetic part}}{\text{Total amount of Fe in reduced sample}} \times 100 \quad (1)$$

$$\% \text{ Mn loss} = \frac{\text{Amount of Mn in magnetic part}}{\text{Total amount of Mn in reduced sample}} \times 100 \quad (2)$$

$$\text{Mn/Fe} = \frac{\text{Content of Mn in non-magnetic part}}{\text{Content of Fe in non-magnetic part}} \quad (3)$$

The effect of particle size on magnetic separation is presented in **Table 3**. It can be observed from the results that the amount of iron removed by magnetic separation increases with decreasing particle but the manganese loss also increases, and that a smaller particle size results in a higher Mn/Fe ratio after magnetic separation. In addition, Table 3 also indicates that, when the particle size is below 105 μm ,

Fig. 4. XRD pattern of magnetic part from preliminary test.

Fig. 5. XRD pattern of non-magnetic part from preliminary test.

particle size has a much smaller effect on magnetic separation. Therefore, the particle size of the sample used in the subsequent tests is no larger than 105 μm .

3.3. The Effect of Reduction Conditions

The effects of such reduction parameters as reduction time, temperature, and the CO content of reducing gas were further determined in this study.

3.3.1. The Effect of Reduction Time

The effect of reduction time was studied at 600°C with a mixture gas of CO and CO₂ (CO/CO₂ = 30/70, Log ($P_{O_2} / P^\ominus$) = -23.99). The test results at different reduction times are summarized in **Figs. 6(a)–6(c)**.

In the reduction time range from 5 to 25 minutes, there is a remarkable increase with the increasing of roasting time in the amount of removed iron and the Mn/Fe ratio after magnetic separation. At the same time, the amount of manganese lost during the magnetic separation also increases slightly from around 3.6 to 4.9%. Further increase in the reduction time beyond 25 minutes has only a small effect on the magnetic separation.

3.3.2. The Effect of Temperature

The effect of temperature was investigated in the range from 400 to 700°C. The sample particle was reduced by a CO–CO₂ mixture (CO/CO₂ = 30/70) for 25 minutes at different temperatures (Log ($P_{O_2} / P^\ominus$): -20.51 ~ -34.06), followed by magnetic separation. The results are presented in **Figs. 7(a)–7(c)**.

It can be observed from these figures that both the weight percent of removed iron and that of manganese loss increase with increasing temperature. A higher temperature also results in a higher Mn/Fe ratio after magnetic separation. It is noted that the effect of temperature is strong below 600°C.

3.3.3. The Effect of CO Content of Reducing Gas

The effect of CO content was studied at 600°C and reaction

Table 3. Effect of particle size.

Particle size (μm)	% Fe removed	% Mn loss	Mn/Fe ratio
500–1 000	19.2	2.9	11.3
210–297	21.2	4.2	10.4
105–150	36.9	4.4	14.5
74–105	45.4	5.1	15.7
62–74	49.5	5.4	16.8
< 45	48.6	5.5	15.9

Fig. 6. The effect of reduction time at 600°C and 30% CO: (a) % Fe removed; (b) Mn/Fe achieved by magnetic separation; (c) % Mn lost.

Fig. 7. The effect of temperature with 25 min reduction time at 30% CO: (a) % of Fe removed; (b) Mn/Fe achieved by magnetic separation; (c) % of Mn lost.

Fig. 8. The effect of CO content at 600°C and 25 min reduction time: (a) % of Fe removed; (b) Mn/Fe achieved by magnetic separation; (c) % of Mn lost.

time of 25 minutes. The CO content of reducing gas was varied from 10 to 40 vol% ($\log(P_{O_2}/P^0)$: $-22.82 \sim -24.37$), and the results are shown in Figs. 8(a)–8(c). It is seen that a high CO content favors the removal of iron and results in a high Mn/Fe ratio after magnetic separation, especially when the CO content changes from 10 to 30 vol%. Meanwhile, the amount of manganese lost during magnetic separation also increases with increasing CO content.

From the above three sets of single-factor experiment, we find that the amount of removed iron and Mn/Fe ratio in the product are improved by increasing reduction time, temperature, and CO content, with a slight increase in Mn loss. Meanwhile, the reduction condition has a smaller effect when the reduction time, temperature, and CO content increase beyond 25 minutes, 600°C, and 30 vol%. Thus, this reduction condition may be considered as the optimum condition, both regarding the efficiency of magnetic separation and cost of operation.

The results of all the single-factor experiments indicate approximately linear relationships up to certain levels of experimental parameters.

3.4. Full Factorial Design for Selective Reduction of “LP” Sample

A full factorial design was used to investigate the significance and interactive effect of each experimental parameter on the magnetic separation. The parameters studied were reduction time, temperature, and CO content of reducing gas. It is envisioned that an industrial application of this upgrading process would be based on the use of CO-containing waste gases from existing operations and without using large amounts of energy. Therefore, the ranges of the three parameters were decided by these considerations together with the test results of single-factor experiments, showing linear relationships within these ranges. Thus, two levels at maximum and minimum values of these variables

were tested and base-level experiments were carried out. The tested levels are listed in Table 4, and the detailed design results, is shown in Table 5.

The effects of different reduction parameters on the efficiency of magnetic separation are expressed by the following equation:

$$Y_i = a_{i0} + a_{i1}X_1 + a_{i2}X_2 + a_{i3}X_3 + a_{i12}X_1X_2 + a_{i13}X_1X_3 + a_{i23}X_2X_3 + a_{i123}X_1X_2X_3 \dots \dots \dots (4)$$

where, Y_1 , Y_2 , Y_3 = weight percent of iron removed by magnetic separation, Mn/Fe ratio of non-magnetic part, and weight percent of manganese lost during magnetic separation, respectively; a_i = empirical model coefficients obtained from base-level tests; X_1 , X_2 , X_3 = reduction time, temperature, and CO content, respectively.

The relationships between coded and actual values of different parameters are given as:

$$X_1 = \frac{x_1 - 15}{10}; X_2 = \frac{x_2 - 500}{100}; X_3 = \frac{x_3 - 20}{10} \dots \dots (5), (6), (7)$$

The regression coefficients are calculated as:

$$a_{i0} = \frac{\sum Y_i}{N}; a_{ip} = \frac{\sum X_p Y_i}{N}; a_{ipq} = \frac{\sum (X_p X_q) Y_i}{N};$$

$$a_{i123} = \frac{\sum (X_1 X_2 X_3) Y_i}{N} \dots \dots \dots (8), (9), (10), (11)$$

where $p=1,2,3$; $q=p+1, \dots, 3$; $p \neq q$.

The coefficient a_{i0} represents the average value obtained from these experiments conducted at base-level as indicated in tests 9–11 of Table 5. Coefficients a_{i1} , a_{i2} , and a_{i3} give the effects of reduction time, temperature, and CO content of reducing gas, respectively. Coefficients a_{i12} , a_{i13} , and a_{i23} refer to the interactive effect of two of the parameters investigated in this work, and a_{i123} shows the interactive effect of all three parameters.

Table 4. Levels of each parameter.

Parameters	Code	Lowest level ($X_i = -1$)	Base level ($X_i = 0$)	Highest level ($X_i = +1$)
Time (min)	X_1	5	15	25
Temperature ($^{\circ}\text{C}$)	X_2	400	500	600
CO content (vol %)	X_3	10	20	30

Table 5. Design matrix and test result of 2^3 factorial experiments.

Test	X_1	X_2	X_3	X_1X_2	X_1X_3	X_2X_3	$X_1X_2X_3$	% Fe removed	Mn/Fe	% Mn lost
1	1	1	1	1	1	1	1	48.7	16.0	5.2
2	1	-1	1	-1	-1	1	-1	25.3	10.8	3.0
3	-1	-1	1	1	-1	-1	1	23.2	12.2	2.6
4	-1	1	1	1	1	1	-1	14.6	11.8	1.8
5	-1	1	-1	-1	-1	1	1	31.0	14.6	3.8
6	1	1	-1	1	-1	-1	-1	33.3	12.4	2.8
7	-1	1	1	-1	1	-1	-1	31.8	12.9	4.2
8	1	-1	-1	-1	1	-1	1	24.2	13.7	2.8
9	0	0	0	0	0	0	0	30.9	12.6	2.8
10	0	0	0	0	0	0	0	31.0	12.5	2.8
11	0	0	0	0	0	0	0	31.0	12.7	2.8

Fig. 9. Comparison of experimental data and relevant data calculated from the regression equations.

Based on these test results, the regression equations, which represent the effects of experimental parameters and their interactions on the efficiency of selective reduction and magnetic separation, are developed as follows:

$$Y_1 = 31.0 + 3.44X_1 + 6.39X_2 + 2.89X_3 + 0.82X_1X_2 + 0.72X_1X_3 + 0.79X_2X_3 + 2.45X_1X_2X_3 \dots (12)$$

$$Y_2 = 12.6 + 0.52X_1 + 1.05X_2 + 0.40X_3 + 0.22X_1X_2 + 0.25X_1X_3 + 0.21X_2X_3 + 0.31X_1X_2X_3 \dots (13)$$

$$Y_3 = 2.8 + 0.34X_1 + 0.74X_2 + 0.21X_3 + 0.12X_1X_2 + 0.08X_1X_3 + 0.03X_2X_3 + 0.26X_1X_2X_3 \dots (14)$$

The three base-level tests give highly consistent results, implying a good reproducibility of the experiments.

From the regression Eqs. (12)–(14), we can learn that within the ranges of different experimental parameters selected, all of the experimental parameters have significant effect on the efficiency of selective reduction and magnetic separation. With increasing temperature, reduction time, and CO content, the amount of removed iron and Mn/Fe ratio achieved by magnetic separation are improved. The amount of manganese lost during the magnetic separation also increases. Among these parameters studied in this work, temperature has the strongest effect in the range tested, followed by reduction time and CO content. In addition, these regression equations also indicate that all of the interaction effects are positive for the removal of iron, improvement of Mn/Fe ratio as well as manganese loss, but the significance of interaction effect is much smaller than the effect of each single experimental parameter. As shown in Figs. 9(a)–9(c), the calculated values, reproduced from the regression equations, are in a good agreement with the experimental data.

4. Conclusions

The ferruginous low-grade manganese ore used in this study was successfully upgraded by the selective reduction by CO followed by magnetic separation.

Under the optimum condition (particle size: $<105 \mu\text{m}$, reduction time: 25 minutes, temperature: 600°C , CO content: 30%) the Mn content in the ore increased from around 36% to more than 45%, rendering a substantial upgrading based on the classification of manganese ore as shown in Table 1. Besides, up to 50% of iron was removed at a Mn loss of around 5% after selective reduction and magnetic separation. As a result, this can not only be beneficial regarding power consumption in the following process due to the enrichment of manganese, but also may lead to a large degree of freedom in mixing the charge for the production of ferromanganese, owing to a relative high Mn/Fe ratio achieved.

In addition, the test results of full factorial experiments indicate that, within the ranges of reduction parameters tested in this work, temperature has the strongest effect, followed by reduction time and CO content.

Acknowledgments

The authors would like to thank POSCO for supplying the manganese ore and for chemical analysis of sample manganese ore. This research was supported by Research Institute of Industrial Science and Technology (RIST), Pohang, Korea.

REFERENCES

- 1) P. W. Harben, J. M. Harris and C. Raleigh: *Manganese Uses & Markets*, Industrial Minerals Information Ltd., London, (1998), Chapter 4, 25.
- 2) Y. V. Swamy, B. Bhoi, S. Prakash and H. S. Ray: *Miner Metall. Proc.*, **15** (1998), 34.
- 3) S. V. Kothari and S. A. Nilkantha: US Patent, 5270022, (1993).
- 4) T. Sharma: *Int. J. Miner. Proc.*, **35** (1992), 191.
- 5) N. Anacleto, O. Ostrovski and S. Ganguly: *ISIJ Int.*, **44** (2004), 1615.
- 6) P. D. Berger and R. E. Maurer: *Experimental Design with Applications in Management, Engineering and the Sciences*, Cengage Learning, Stamford, (2002), Chapter 11, 314.