

HIGH PURITY Mn METAL FROM Mn OXIDE DUST PRODUCED DURING FeMn REFINING PROCESS

Kwang J. Lee, Dong S. Min, Chan S. Park, Young K. Park, Hae C. Jo, Seong H. Hong

Dongbu Metal Co., Donghae, Gangwon-do, Korea; lkj0718@dongbu.com

ABSTRACT

During pneumatic oxygen refining process of MC and LC FeMn alloys, about 8% of Mn element is lost by evaporative mechanism as dust which is comprised of 67% Mn in the form of manganese oxides. Because of its high economic value, Mn dust from the refining process has been pelletized and recycled to FeMn smelting furnaces in order to recover the Mn value. Some of the dust has been marketed in the applications of soft ferrite, lubricant in oil drilling, and pigment for refractory. However, these practices did not produce enough rewards to justify these reclaiming activities of Mn value.

In order to recover the high Mn value, a process was developed to produce a high purity Mn metal from the dust. The process is based on an alumino-thermic reduction of Mn dust. Mn dust is mixed with aluminium and lime, and the mixture was placed in a magnesia lined iron pot. An ignitor was placed on top of charge mix. When it was ignited, a molten pool of metal and oxide was formed at the location of ignition. These molten mass triggered the thermic reaction in the surrounding area. This thermic reaction self-propagated quickly through the entire pile of mixture. At the end of thermic reaction, the reactor was observed to be covered by a molten layer of slag. A visual observation after cooling showed that the mass consisted of two layers, slag on top and metal in the bottom. The slag layer was separated cleanly from metal. No metallic inclusions were observed in slag layer. The Mn metal contained higher than 90% Mn, and the recovery of Mn was higher than 86%.

1 INTRODUCTION

At present, producers of FeMn alloys face a situation of dwindling supply of high quality Mn ore and, consequently, unstable supply of Mn ores in near future. Also, the global community demands a conservation of natural resources and clean environment. A response from FeMn alloys industry is to conserve Mn unit in the smelting and refining processes as much as possible.

The refined FeMn alloys, medium and low carbon grades FeMn, are produced by de-carburizing high carbon FeMn alloy using a technology of gaseous oxygen blowing. Because of its high volatility, however, about 8% of Mn element in HC FeMn alloy is lost as Mn oxide dust during the pneumatic oxygen refining process. Because of the government regulation on particulate discharge, Mn oxide dust is recovered currently by cyclone and bag filter dust collectors. It contains about 67% Mn, and its high content of Mn indicates that it can be considered as a by-product of high quality raw materials. In spite of its high economic potential, it has been agglomerated and returned to smelting units of FeMn alloy processes or marketed for the applications of soft ferrite, oil drilling, and coloring agents of refractory. The economic rewards, however, have not been satisfactory from these applications. Dongbu Metal, instead, examined various technologies to recover a high economic value from Mn oxide dust and developed the process producing high quality Mn Metal from it.

2 CHARACTERIZATION OF Mn OXIDE DUST

The refining process for medium and low carbon FeMn alloy is based on the de-carburizing reaction of high carbon FeMn alloy by gaseous oxygen. As the de-carburizing reaction progresses, the melt temperature increases. At the same time, Mn element in melt begins to evaporate and is oxidized to Mn oxide by the available oxygen after accounting for decarburizing reaction. Also, the volatility of Mn element increases with increasing melt temperature. Thus formed Mn oxide dust as fine particles is carried away by exhausting CO gas from the reactor. After passing through a cooler, the Mn oxide

dust bearing exhaust gas is introduced to cyclone and bag filter dust collectors in order to separate particulate matters from discharging gas. The collected Mn oxide dust is made of fine powder and has brown color. Both cyclone and bag filter dusts have same general appearance, but cyclone dust contains coarser particles than bag filter dust does.

2.1 Chemical Analysis of Mn Oxide Dust

The representative samples were collected from both cyclone and bag filter dusts for their chemical analysis. Table 1 shows the results.

Table 1: Chemical analysis of Mn oxide dust, wt%

Mn oxide dust	Mn	SiO ₂	CaO	Al ₂ O ₃	MgO	Fe	C	P	S
Cyclone	61	2.75	6.02	0.23	0.14	5.95	0.29	0.051	0.018
Bag filter	67	1.60	0.28	0.26	0.15	3.44	0.08	0.038	0.025

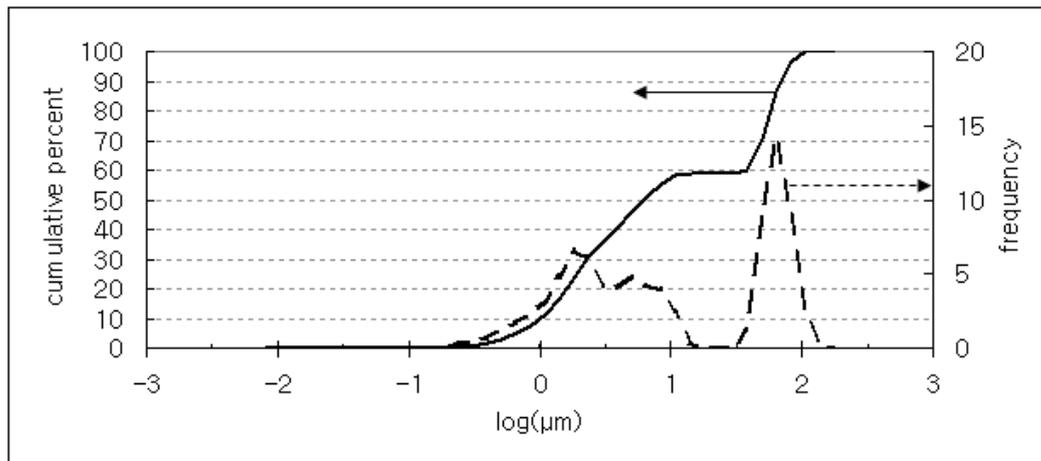
It showed that bag filter dust contained higher Mn than cyclone dust does and the former has lower contents of SiO₂, CaO, Fe, C, and P than the latter does. The contents of SiO₂ and CaO appear to be originated from fractured agents used for reducing MnO at the end of de-carburization period. Fe, C, and P are considered to come from ejected FeMn droplets during de-carburizing reaction. In general, Mn oxide dust from bag filter dust collector is a higher quality by-product than that from cyclone dust collector.

2.2 Particle Size Analysis of Mn Oxide Dust

Mn oxide dusts recovered by cyclone and bag filter collectors were analyzed for their particle size distribution and cumulative percentage with the use of a laser particle analyzer (FRITSCH) which has a detective range of 0.1 to 300 μm. Figure 1 shows the result.

The cyclone Mn oxide dust, Figure 1 (a), is shown to be constituted of two particle size groups, 0.1 - 20 μm and 40 - 200 μm. The smaller sized particle group shows a tendency of bimodal distribution. A distinctive separation of two particle size groups suggests that they may have different origins. It is suspected that the larger particle size group may come from the fragmentation of added reducing agents and slag and alloy formed during the de-carburization period and that the smaller size group from the dust generated by evaporation of Mn and some other fine particles. In contrast to this, the bag filter Mn oxide dust as shown in Figure 1 (b) has a particle distribution in the size range of 0.1 to 100 μm but does not contain particles larger than about 100 μm. The particles in the size range of 0.1 to 100 μm have the same characteristic bimodal distribution observed with the smaller sized particle group in the cyclone Mn oxide dust. This behavior of bimodal distribution suggests that the smaller sized particle group in both Mn oxide dusts is generated by the same mechanism. This aspect will be examined further in the followings. In general, the particle size of bag filter Mn oxide dust is finer than that of cyclone Mn oxide dust.

(a) cyclone dust



(b) bag filter dust

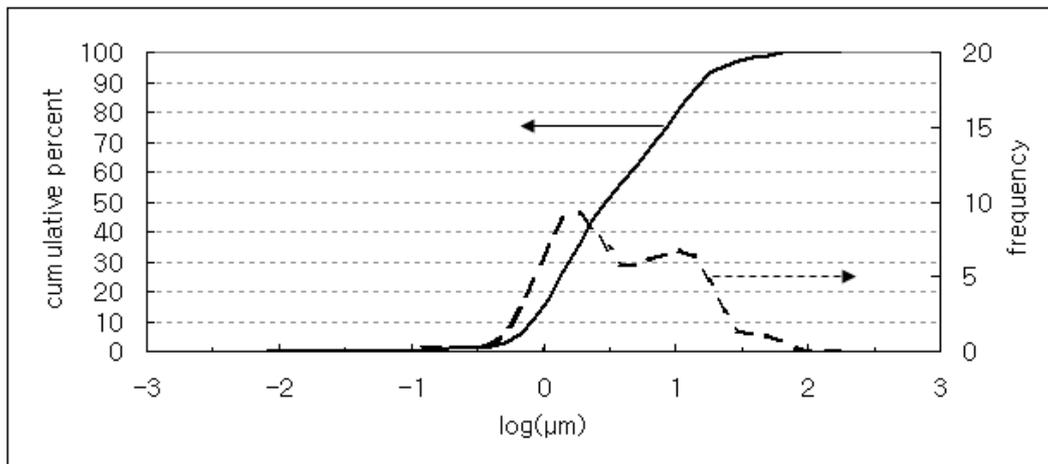


Figure 1: The particle size distribution of Mn oxide dusts (a) cyclone dust and (b) bag filter dust

2.3 SEM Examination of Mn Oxide Dust

The cyclone Mn oxide dust was examined by SEM. Figure 2 shows its back scattering SEM image. It shows, generally, to consist of three different size groups, about 300 μm , 30 to 150 μm , and finer particles, the size of which can not be resolved in this image. The information of EDAX indicates that the particle with the size of 300 μm has an aspect ratio greater than unity and is Mn silicate. This must come from slag formed during the refining process. The particles with the size in the range of 30 to 150 μm has the aspect ratio of near unity and is shown to be (Mn, Fe) oxides. The aspect ratio of unity suggests that they may be oxidized droplets of FeMn alloy. The EDAX information shows that the finer particles are Mn oxides. Although it is not shown here for the reason of brevity, a fragmented CaO particle in the size of about 500 μm was observed in cyclone Mn oxide dust from other SEM examination.

Figure 3 shows the back scattering SEM image of bag filter Mn oxide dust. It composes of two different particle sizes, about 40 μm , and about less than 1 μm . Their aspect ratios appear to be one. The information of EDAX shows that the larger particles are (Mn, Fe) oxides and the finer particles Mn oxide. The (Mn, Fe) oxides have the same geometrical as well as chemical features observed with the particles in the cyclone Mn oxide dust. It indicates that (Mn, Fe) oxides may be resulted from

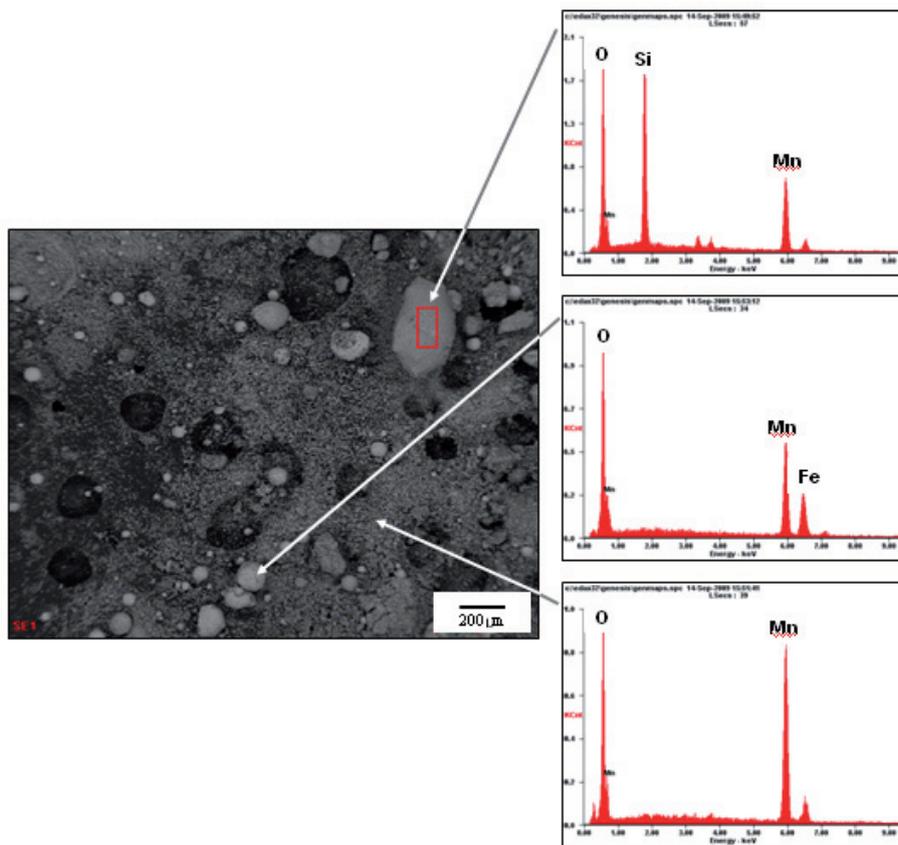


Figure 2: SEM examination of cyclone Mn oxide dust

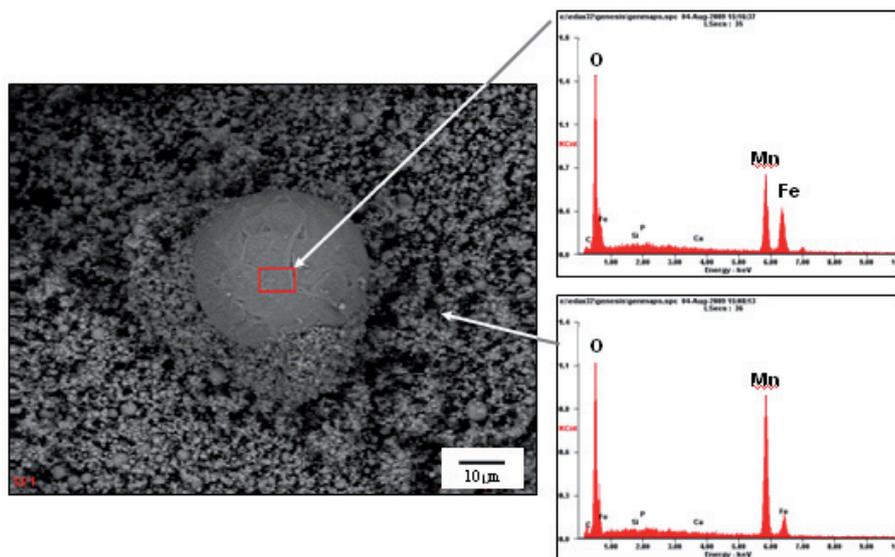


Figure 3: SEM examination of bag filter Mn oxide dust

oxidation of droplets of FeMn alloy in both cases. The particle less than 1 μm is shown to be Mn oxide, and they are considered to be formed by oxidation of evaporated Mn.

2.4 XRD Analysis of Mn Oxide Dust

Bag filter Mn oxide dust was examined by XRD. Figure 4 shows the result. It consists of Mn_3O_4 and MnFe_2O_4 . It is apparent that Mn oxide identified by SEM (Figure 2 & 3) is Mn_3O_4 and that (Mn, Fe) oxides is MnFe_2O_4 .

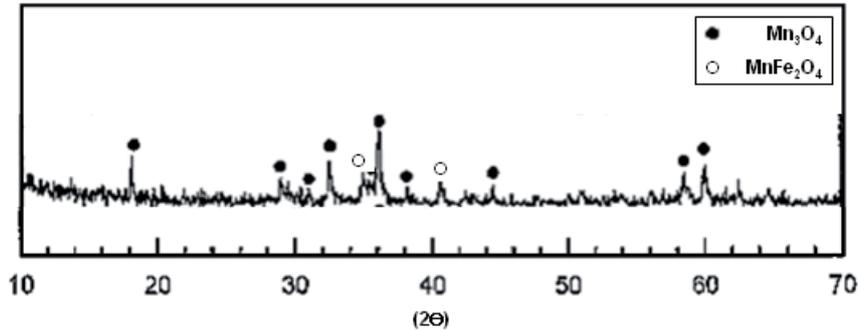


Figure 4: XRD analysis of bag filter Mn oxide dust

All experimental evidences discussed above sections indicate that the bag filter Mn oxide dust consists of Mn_3O_4 which is formed by oxidation of evaporated Mn and that MnFe_2O_4 which is oxidized FeMn alloy droplets. It is clear that bag filter Mn oxide dust is a high purity by-product and can be a good candidate for the production of high purity Mn Metal.

3 CANDIDATE PROCESSES FOR HIGH PURITY Mn METAL

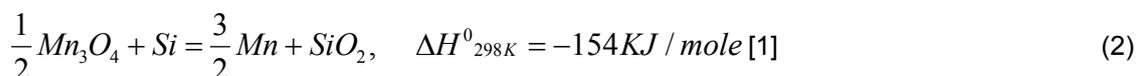
The processes utilizing by-products are desired to have low capital investments and, at the same time, to meet the necessary chemical specifications for high purity Mn metal. The processes can be evaluated by considering reducing reactions of Mn oxide dusts with various reducing agents. The candidate reducing agents are C, Si, and Al.

The reducing reaction by carbon may be described by the following equation (1).



This reaction is shown to be endothermic. It requires an externally fed energy source for the reaction to proceed according to the equation (1). It suggests that the carbo-thermic reduction process may demand a considerable capital investment. The impurities such as P and S can be maintained at low levels as long as their intake is suppressed. However, carbon has a strong affinity to Mn, and it is difficult to limit its content to less than 1wt% C in Mn, while maintaining Mn recovery at reasonable level. The carbon content in steel products requiring the use of Mn metal, usually, is far less than 1wt% C. The consideration of this restriction in C specification indicates that the carbo-thermic production of high purity Mn metal may not be suitable.

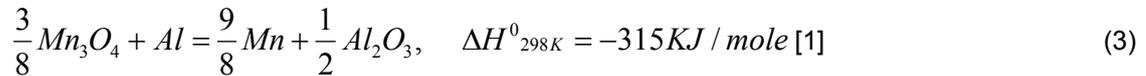
The reducing reaction by silicon may be proceeded by the following equation (2).



The reaction is mildly exothermic. However, its extent is not sufficiently high enough for the reaction to proceed without external supply of energy. Although, its energy account is better than that of carbo-

thermic process, the silico-thermic process, still, may require a substantial capital investment for external energy supply. The control of impurities such as P and S is same as the case for the carbo-thermic process. Because of it's a high affinity to Mn, however, it is difficult to control the content of Si to less than 1wt% Si in Mn at a reasonable recovery of Mn. Again, the steel product requiring the addition of Mn metal, usually, is specified Si content to far less than 1wt% Si, and the silico-thermic process does not appear to be attractive.

The reducing reaction by aluminium may be expressed by the following equation (3).



This reaction is exothermic. Its heat content appears to be self-sufficient to proceed the reducing reaction as described by equation (3) without an external energy supply, and its capital investment is expected to be low. The residual content Al in Mn may be controlled to less than 1wt% Al with a reasonable recovery of Mn. The steel makers practice the deoxidation of steel by Al, and the Al content at about 1wt% in Mn metal is acceptable.

The above analysis indicates that the alumino-thermic reducing process of Mn oxide dust is suitable for the production of high purity Mn metal, and its feasibility is discussed in the following sections.

4 PILOT SCALE TESTS FOR ALUMINO-THERMIC PROCESS

The alumino-thermic reaction of Mn oxide dust, if it proceeds as described by the equation (3), produces Mn metal and Al₂O₃. If Mn metal does not separate from Al₂O₃ slag, the Mn recovery will be suffered. In order to attain a good recovery of Mn, the Mn metal and Al₂O₃ based slag should maintain their fluidity at a sufficiently high level. The exothermic heat from alumino-thermic reaction is expected to be sufficiently high to form liquid Mn alloy but may not be high enough to form a fluid Al₂O₃ slag. Therefore, the process may require fluxing agents for conditioning the fluidity of slag.

The information of the phase diagram of Al₂O₃ and CaO[2], Figure 5, shows that the liquidus decreases from the melting point of Al₂O₃(2053°C) to 1413°C with the addition of CaO to 49% CaO. Based on this information, this study adjusts the slag composition with the addition of CaO in order to attain a fluid slag.

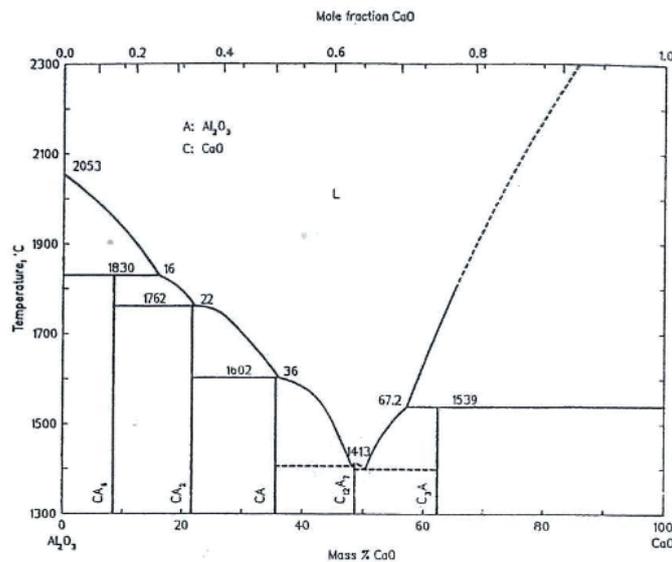


Figure 5: The phase diagram of Al₂O₃-CaO system[2]

It is unavoidable for slag to dissolve MnO. Mn and Al will distribute between alloy and slag, and the distributions of them determine the processing efficiency. In the absence of their specific information, the distribution of Mn and Al may be experimentally determined by changing the ratio of Al to Mn₃O₄ in raw materials.

4.1 Raw Materials

This study uses the bag filter Mn oxide dust because of its high Mn content and low impurity levels. Their relevant information was discussed above.

CaO as fluxing agent was taken from industrial grades lime. Table 2 shows its chemical analysis

Table 2: Chemical analysis of lime, wt%

CaO	SiO ₂	C	S
92.0 min	1.0 max	0.10 max	0.080 max

Al powder sized less than 200mesh was used as reducing agent. Its chemical analysis is shown in Table 3.

Table 3: Chemical analysis of Al powder, wt%

Al	Si	C	P
99.0 min	0.5 max	0.010 max	0.0030 max

4.2 Mix Order

The mix order for this study was prepared based on 50kg of bag filter Mn oxide dust. Al powder as a reducing agent was varied as the weight ratio of Al to Mn in Mn oxide dust in the range of 0.44 to 0.52. The lime was added at 20% of the weight of Mn oxide dust. These ingredients were mixed thoroughly.

In order to help starting reaction, an ignitor was prepared with Mg powder.

4.3 Procedure of Pilot Scale Tests

A batch of raw materials was prepared by mixing 50kg of bag filter Mn oxide dust with lime and Al powder in the proportion as specified above and was charged into a MgO lined iron pot.

An ignitor was placed in the central location at the top of the batch in an iron pot. When it was ignited, the ignitor was burned with a whitish smoke. A portion of charged materials in the immediate vicinity of the ignitor was melted and reacted exothermically. It appears that Al powder was melted by the heat from the burning Mg in the ignitor and that the molten Al facilitated the exothermic reaction. The generated exothermic heat from the initial reaction triggered exothermic reaction of charged materials adjacent to the initial reaction site. In this manner, the exothermic reaction propagated out radially in increment and sustained until it reached to MgO lining of iron pot. This took about 3 minutes. As a whole, the reaction proceeded calmly. At the conclusion of exothermic reaction, the top surface of the content in the iron pot was flat and smooth, indicating that the content was molten.

After cooling, the content of iron pot was taken out, and it was splitted in half. Figure 6 shows its vertical cross section. A visual examination of it shows that metal is separated cleanly from slag and that the slag did not contain any metal droplets. The analysis of Mn metal at Al addition of kgAl / kgMn in Mn oxide dust = 0.47 was 90%Mn, 1%Al, 0.1%C, 0.05%P, and 0.02%S.

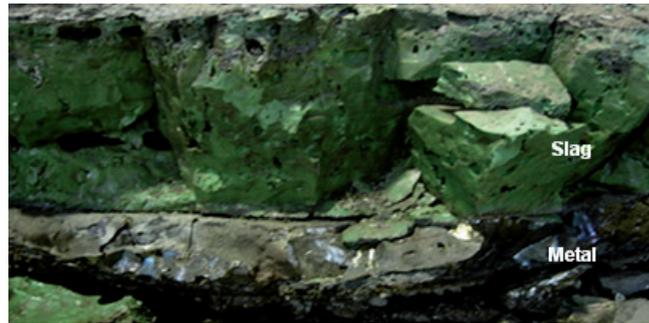


Figure 6: The vertical cross section of the content in iron pot

5 DISCUSSION

The characteristics of alumino-thermic reactions can be assessed by examining distribution ratio of Mn and Al between slag and metal.

The distribution ratio of Mn, $L_{Mn} = (\%MnO) / [\%Mn]$, was related with the ratio of Al powder to Mn oxide dust, kgAl / kgMn in Mn oxide dust. Figure 7 shows the relationship. The distribution of Mn decreases with increasing Al in raw materials. This is due to the increased reduction of Mn oxide with increasing addition of Al.

The distribution ratio of Al, $1 / L_{Al} = [\%Al] / (\%Al_2O_3)$, as presented in Figure 8 shows that the residual Al content in Mn metal increases with increasing addition of Al.

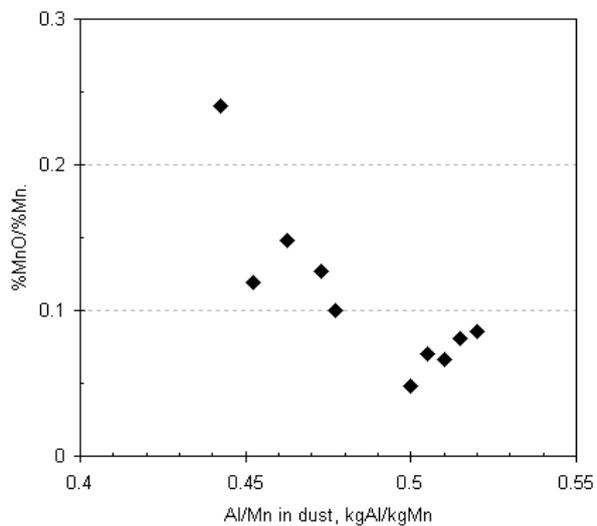


Figure 7: Distribution of Mn between metal and slag

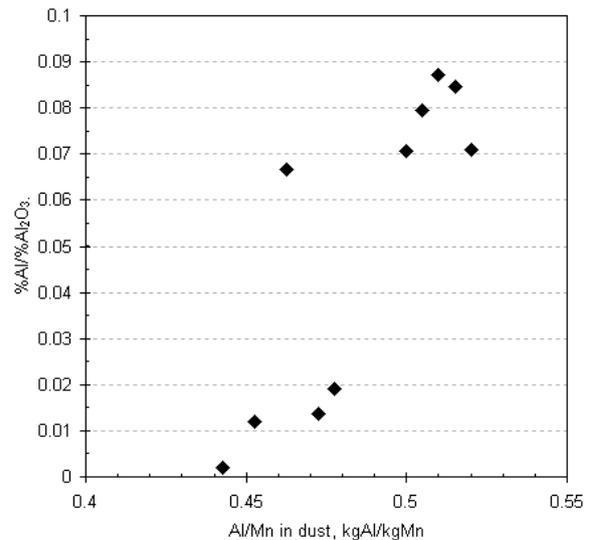


Figure 8: Distribution of Al between metal and slag

It indicates that an increasing addition of Al results in an increasing recovery of Mn and an increasing residual Al content in Mn metal. This relationship is shown in Figure 9. The Mn recovery increases quickly with increasing Al addition in the range of kgAl / kgMn in Mn oxide dust = 0.44 – 0.47. The residual Al content increased slowly with increasing Al addition in the same range. When the addition of Al increases beyond kgAl / kgMn in Mn oxide dust = 0.47, the Mn recovery increases slowly while the residual Al content increases quickly with the increasing addition of Al. These transitions take place with Mn recovery at 86% and residual Al content at 1%Al in Mn metal.

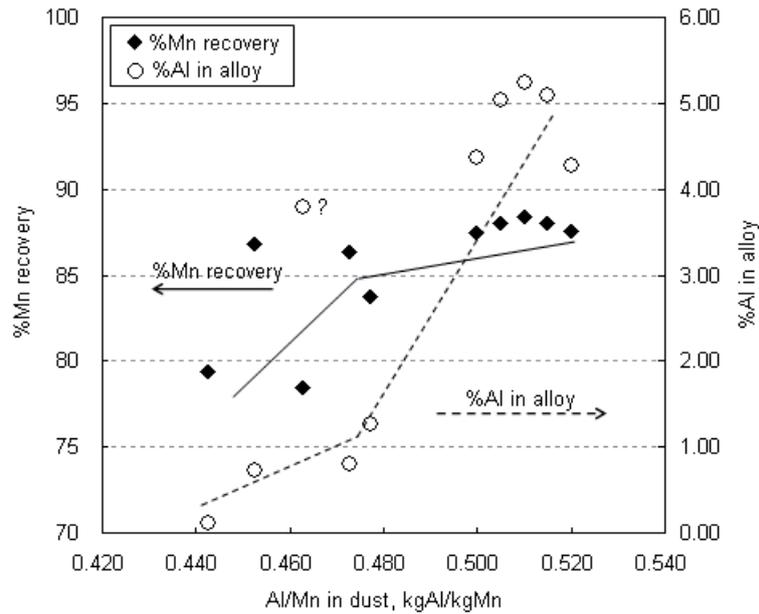


Figure 9: Variation of %Mn recovery & %Al in alloy with kgAl / kgMn in Mn oxide dust

6 CONCLUSIONS

Bag filter Mn oxide dust can be processed alumino-thermally to produce a high purity Mn metal. The alumino-thermic process can be operated safely with a minimum capital investment. The Mn recovery increases with the increasing addition of Al in raw materials. However, the residual Al content in Mn metal also increases with increasing addition of Al. Mn metal with 1wt% Al can be produced by alumino-thermic reaction of bag filter Mn oxide dust with a Mn recovery of 86%.

7 REFERENCES

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- [2] Slag Atlas, 2nd edition, Stahleisen, 1995, p. 39.

