

UPGRADING OF Mn / Fe RATIO OF LOW-GRADE MANGANESE ORE FOR FERROMANGANESE PRODUCTION

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ABSTRACT

The Mn / Fe ratio is crucial in producing the commercial ferromanganese grade in a submerged electric furnace. Huge amounts of low-grade manganese ores are located in many countries around the world. These deposits are only partially used in ferromanganese production. The ores contain large quantities of iron and thus the Mn / Fe ratio is low, 3 - 4. Iron appears partially in ore as individual hematite and goethite grains and the remainder of it is in the manganese grains. The laboratory tests showed that the Mn / Fe ratio increased up to 11 when the pre-reduction of ore was performed in a laboratory rotary kiln at about 800°C. The pre-reduction was performed in a reducing gas atmosphere and with solid carbon. The product from the kiln contained individual magnetite grains, which were separated after grinding by a magnetic separation method. The non-magnetic fraction requires pelletizing and sintering in a separate process step to produce durable and porous pellets, which are excellent raw material for ferromanganese smelting.

1 INTRODUCTION

During the 1990s, Outotec Research Center (former Outokumpu Research Center) was commissioned by Sandur Manganese & Iron Ores Ltd to research the possibility of upgrading low-grade manganese ore (Mn/Fe ratio ~ 3) to a viable raw material for ferromanganese production. This manuscript is based on a laboratory test performed for the Sandur Manganese study [1]. The first step of the study was to make the chemical and mineralogical analyses of the manganese ore. The mineralogy was studied with a scanning electron microscope and the object was to find out how iron is distributed in the ore.

The second step was pre-reduction and magnetic separation of the product. The study showed that Mn/Fe ratio could be raised to about 11-12, which is actually too high, but can be reduced to an appropriate level => 8.

There are few publications concerning the enrichment of low-grade manganese ore using solid reductant. Swamy et al. [2] studied this phenomena with TGA tests. They found that the optimum pre-reducing temperature for increasing the Mn/Fe ratio of the ore non-magnetic part would be 850°C, and they also observed that a finer particle size (-0.15mm) gave a better Mn/Fe ratio compared to the coarser ore (-6 to +3 mm). Rudramuniyappa et al. [3] reported that reduction roasting followed by magnetic separation is considered to be the best method for upgrading the Chikkanayakanahalli manganese ores. They also showed that tabling studies carried out were not encouraging, probably due to the similar behavior of Mn and Fe. Rao et al. [4] reported, that in reduction roasting of low-grade manganese ore followed by magnetic separation, 60 % of phosphorus can also be removed.

After these tests Outotec has also continued studies into the pre-treatment of different manganese ores. Based on these studies, a process flowsheet for the industrial-scale production of upgraded manganese ore has been developed.

2 TESTS AND RESEARCH PERFORMED

Two different iron-rich Mn-ore samples were received. In this stage, the following issues were studied:

- Mn-ore chemical analysis and mineralogy
- Pre-reduction tests in the induction furnace with the 225 ml crucible
- Pre-reduction test in the laboratory-scale rotary kiln using different temperatures
- Structural analyses of the different products
- Magnetic separation tests and analyses of the products

Iron can be separated from the ore selectively and the ore with a higher Mn/Fe-ratio can be produced in two ways:

- Moderate Fe_2O_3 and $\text{FeO} \cdot \text{OH}$ reduction to magnetite at low temperature, below 800°C
- Strong reduction of iron oxides to a metallic phase at high temperature, around 1000°C

The latter separation method can be difficult to carry out in a full-scale process.

3 RESULTS

3.1 Ore chemical analysis and structure analysis

From two Mn ores, A- and C-grade, representative samples were taken for the chemical analysis and structure analysis. The structure was studied with a microscope, a microanalysator and a diffractometer. The focus of these studies was to find out: where iron compounds are located, in which form, and how iron is bound to Mn. The role of aluminium was also studied, since it is an important factor affecting the slag amount in the smelting stage. Chemical analyses of the raw materials are shown in Table 1. Correspondingly, Mn-ore phases in raw materials are shown in Table 2 and examples of Mn-ore phase analyses in Table 3.

Generally, Mn appears in the following main compounds:

- MnO_2
- $\text{KMn}_8\text{O}_{16}$
- MnOOH

Dominant phases in both ores are MnO_2 and $\text{KMn}_8\text{O}_{16}$, but MnO_2 seem to be missing from grade C ore.

The microstructure of Grade A ore is shown in Figures 1 and 2, and the microstructure of Grade C is respectively shown in Figures 3 and 4.

Table 1: Raw material analyses, weight %.

Element	Grade 'A'	Grade 'C'
Mn	42.7	34.8
Fe_{tot}	12.6	18.2
Fe^{2+}	<0.1	<0.1
SiO_2	1.7	1.7
Al_2O_3	6.3	9.7
CaO	0.09	0.11
MgO	0.03	0.13
Na	0.03	0.05
K	0.67	0.52
Ba	<0.1	<0.1
S	0.01	0.01
C	0.02	0.07
P	0.002	0.002
H_2O , comb	5.7	7.8
Volatiles _{tot}	14.5*	15.4*
Mn/Fe	3.4	1.9
O/Mn	1.97**	1.87**

*Hydroxide H_2O . Oxygen O_2 , which is thermically decomposed from MnO_2 .

**Calculated total composition to 100 % first.

Table 2: Mn-ore phases in raw materials.

Element	Grade 'A'	Grade 'C'
MnO ₂ , pyrolusite	X	-
KMn ₈ O ₁₆ , cryptomelane	X	X
MnO(OH), groutite	X	X
Ca ₂ Mn ₃ Si ₃ O ₁₀ (OH) ₄ , orientire	X	X
Na(Ca) ₂ Mn ₈ O ₁₆ , sodium or calcium manganese oxide	X	X
Mn(OH) ₂ , pyrochroite	X	X
FeO(OH), goethite	X	X
Fe ₂ O ₃ , hematite	X	X
Al(OH) ₃ , bayerite		X
(Mg, Al) ₃ (Si, Al) ₂ O ₅ (OH) ₄ , lizardite	X	X
MnO _{1.88} , manganese oxide		X
Al ₂ Si ₂ O ₅ (OH) ₈ , kaolinite		X

Table 3: Examples of Mn-ore phase analyses (weight %).

Compound	Fe	Mn	Al	Si	K
Fe ₂ O ₃	66	2	0.5	0.8	-
Fe ₂ O ₃ – not pure	55	9	3	1.5	0.3
MnO ₂ -KMn ₈ O ₁₆	little	68	0.7	0.3	1.3
Mn, Al, (Fe)-oxide	-	46	17	0.6	-
Hydrated	4	60	3	0.2	1.8
	4	40	17	2.5	-
	16	34	14	0.5	-
	1	0.5	22	26	0.1

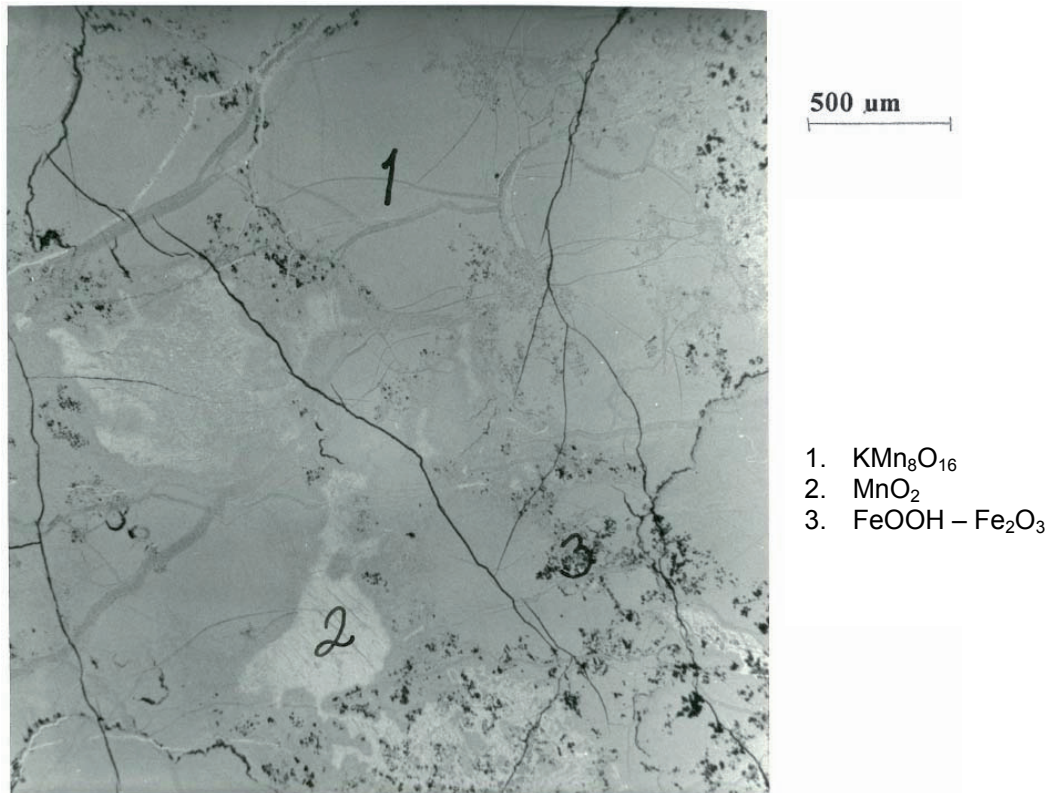


Figure 1: Microstructure of ore, Grade A.

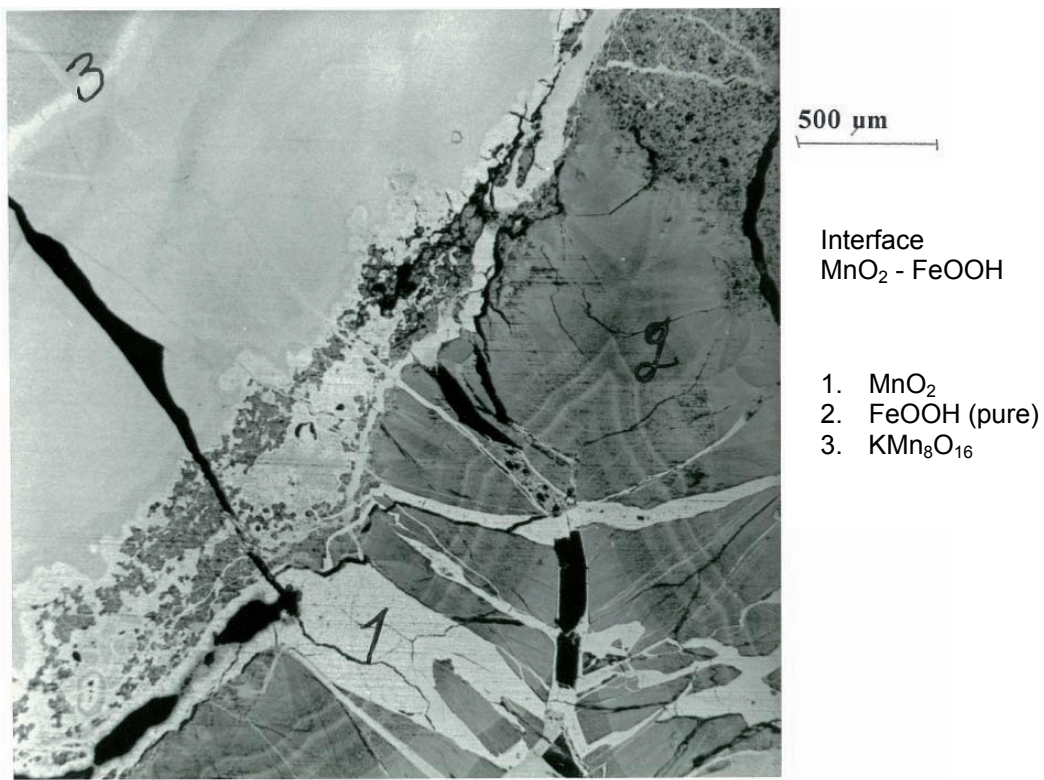


Figure 2: Microstructure of ore, Grade A.

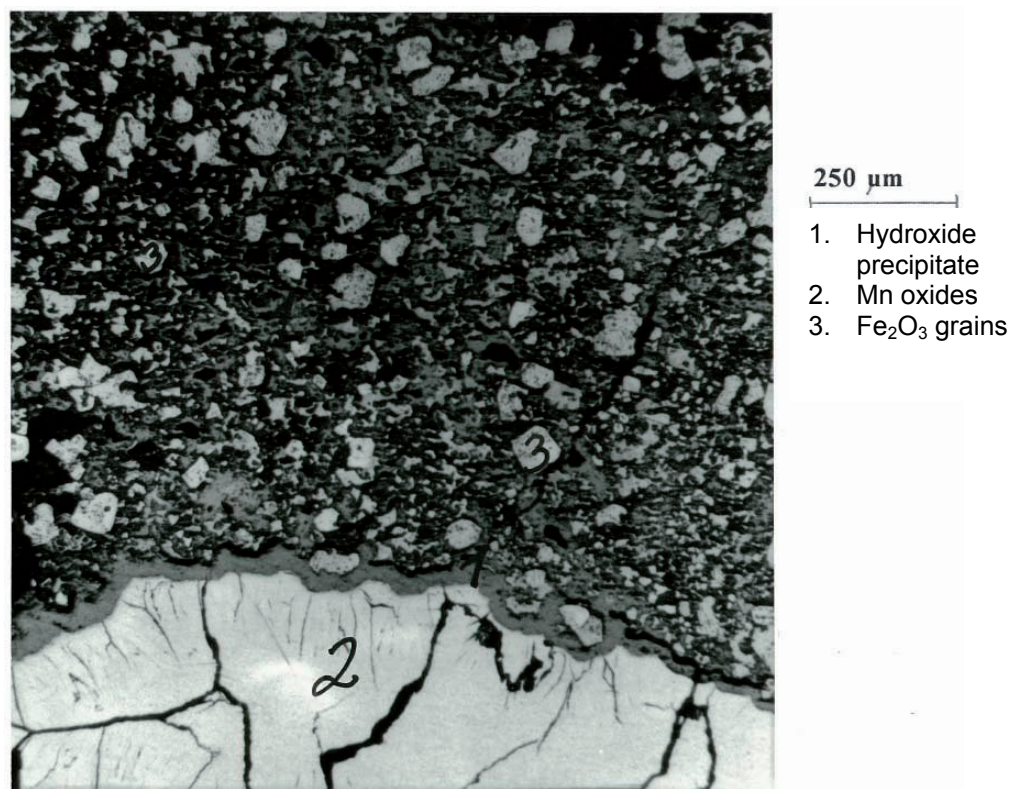


Figure 3: Microstructure of ore, Grade C.

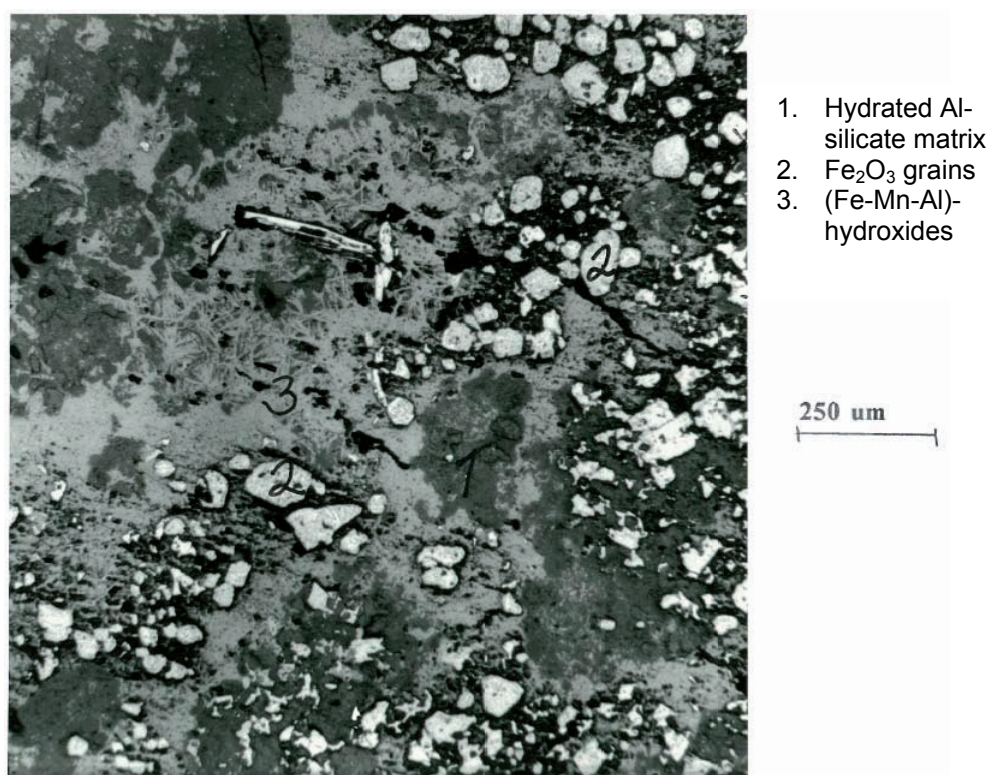


Figure 4: Microstructure of ore, Grade C.

3.2 Pre-reduction in induction furnace

The pre-reduction tests in crucible (225 ml) indicated that the reduction temperature can be up to 900°C, before formation of metallic iron starts. If the temperature is further increased, the minimizing of the Mn losses to magnetic fraction becomes difficult.

3.3 Pre-reduction in rotary kiln

These tests were performed in a laboratory-scale rotary kiln. Mn ore grade A and grade C were mixed in a proportion of 1:1, and the total ore amount was 1000 g. Coke addition to the feed blend was 176g. The amount of coke was selected to be overstoichiometric, because of the small scale and carbon losses due to Boudouard reaction. The feed blend was crushed to a size of below 1.7 mm, and the reductant coke grain size was max. 2.4 mm. The rotary kiln atmosphere was achieved with a small gas flow, 3 l/min, to the kiln.

Two different temperatures were used in tests: 800°C (magnetic area for iron) and 1000°C (metallization area for iron). Retention time was 0.5 hours and cooling was made in an argon atmosphere. The following Mn-phases are decomposed in the pre-reduction: Pyrolusite, cryptomelane, groutite, pyrochroite. The product phases of reduced ores are shown in Table 4.

Table 4: Product phases of reduced ores.

Test number	Temperature	Atmosphere (N ₂ /CO, Vol-%)	Phases
1	800°C	80/20	Fe ₃ O ₄ , MnFe ₂ O ₄ MnO, Mn ₃ O ₄ , Mn ₂ O ₃ Mn _{0.983} *Fe _{0.017}) ₂ O ₃
2	1000°C	80/20	MnO, MnA ₁₂ O ₄ MnSiO ₂ , Fe _{met}

In the product, which was pre-reduced at 800°C, iron was in Fe₃O₄ form and also as jacobite (MnFe₂O₄). Other Mn – Fe – oxide forms were also present.

The microstructure of the pre-reduced product (800°C) is shown in Figure 5.

In the product, which was pre-reduced at 1000°C, iron was in the form of Mn – Fe – oxides and metallic iron.

3.4 Grinding

Pre-reduced products were ground dry in a laboratory-scale mill to two different fractions (a and b). The dry sieving results for ground-reduced ores are shown in Table 5.

Table 5: Dry sieving results for ground reduced ores.

	Passing 74 µm sieve
Product 1 a) Pre-reduction temperature 800°C	54 %
Product 1 b) Pre-reduction temperature 800°C	69 %
Product 2 a) Pre-reduction temperature 1000°C	50 %
Product 2 b) Pre-reduction temperature 1000°C	72 %

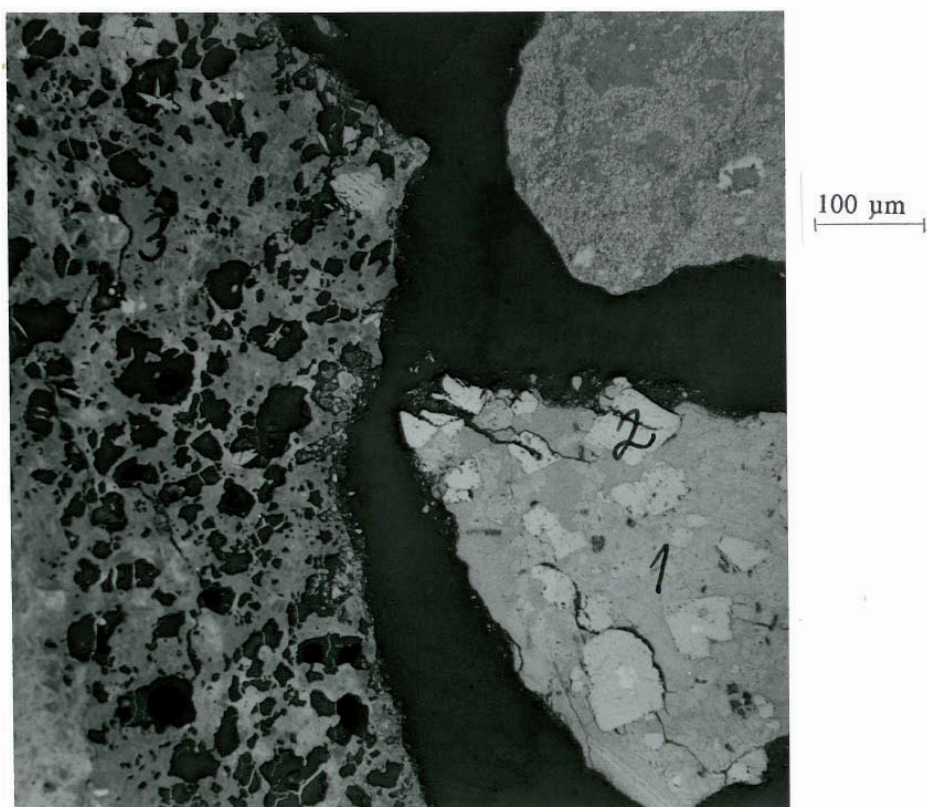
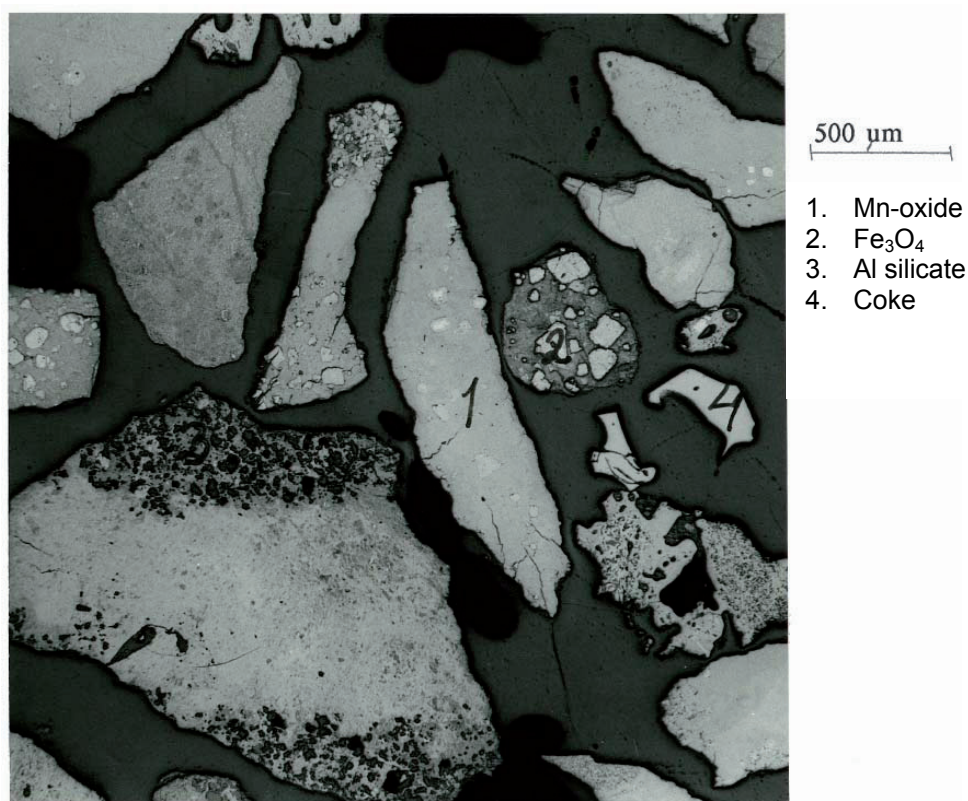


Figure 5: Microstructure of reduced product. Pre-reduction temperature 800°C.

3.5 Magnetic separation

After pre-reduced products were ground, magnetic separation was performed with an inclined magnetic spout. The size of the magnetic spout was 50 x 3000 cm and it consisted of five different magnitude magnetic fields (M1, M2, M3, M4, M5). Magnetic separation for products of lower pre-reduction temperature (800°C) gave promising results and these results are shown in Table 6.

Table 6: Results of magnetic separation.

Element	Pre-reduction temperature 800°C, 54 % -74 µm			Pre-reduction temperature 800°C, 69 % -74 µm		
	M1	M4	Non M.	M1	M4	Non M.
Fe	33.8	17.5	4.3	34.5	20.2	4.7
Mn	31.1	48.4	54.3	29.9	46.9	54.4
SiO ₂	1.5	1.6	3.6	1.5	1.7	3.1
Al ₂ O ₃	5.3	6.9	9.6	4.7	6.8	9.6
CaO	0.3	0.3	0.4	0.3	0.3	0.4
MgO	1.1	<1.0	1.4	<1.0	<1.0	<1.0
C	(0.2)	(0.2)	(22.6)	(0.2)	(0.3)	(21.3)
Mn / Fe	0.9	2.8	12.7	0.9	2.3	11.6
O/Mn*	1,55	1,25	1,59	1,70	1,13	1,61
Satmagan	43	19	4	46	22	5
Mn recovery	25.8	12.6	61.6	21.4	13.3	65.3
Fe recovery	74.8	12.3	12.9	68.5	15.9	15.6

Note for Table 6: In these analyses, carbon has been reduced and the results are shown accordingly.

*Calculated total composition to 100 % first.

Non-magnetic fraction Mn / Fe ratio increased to high levels after magnetic separation in both sizes of fractions (marked in yellow in Table 6).

Magnetic separation for products of higher pre-reduction temperature (1000°C) was found not to be appropriate for selective separation and the Fe/Mn ratio could not be increased for this material.

4 INDUSTRIAL-SCALE PROCESS FLOWSHEET

The industrial scale process flowsheet, based on the studies performed by Outotec is described in figure 6.

Low-grade manganese ore is first crushed to the grain size of -1...5 mm, depending on the characteristics of the ore, to create proper conditions for the next phase. After crushing, the ore is charged with coke or coal in a rotary kiln. In the rotary kiln, iron components are reduced mainly to magnetite at a temperature of 700 – 1000 °C. This temperature provides optimal conditions for the production of a non-magnetic phase with the desired Mn/Fe ratio and high manganese recovery.

The product of the kiln is cooled and ground to a fineness of 50-80% -0,074 mm. Then the magnetic fraction is separated by magnetic separation. The non-magnetic fraction contains high Mn/Fe-ratio material and a certain amount of excess carbon from which the required amount can be separated and recycled back to the process. The product is a fine-ground, pretreated manganese ore, which can be pelletized to make a good raw material for manganese alloy smelting.

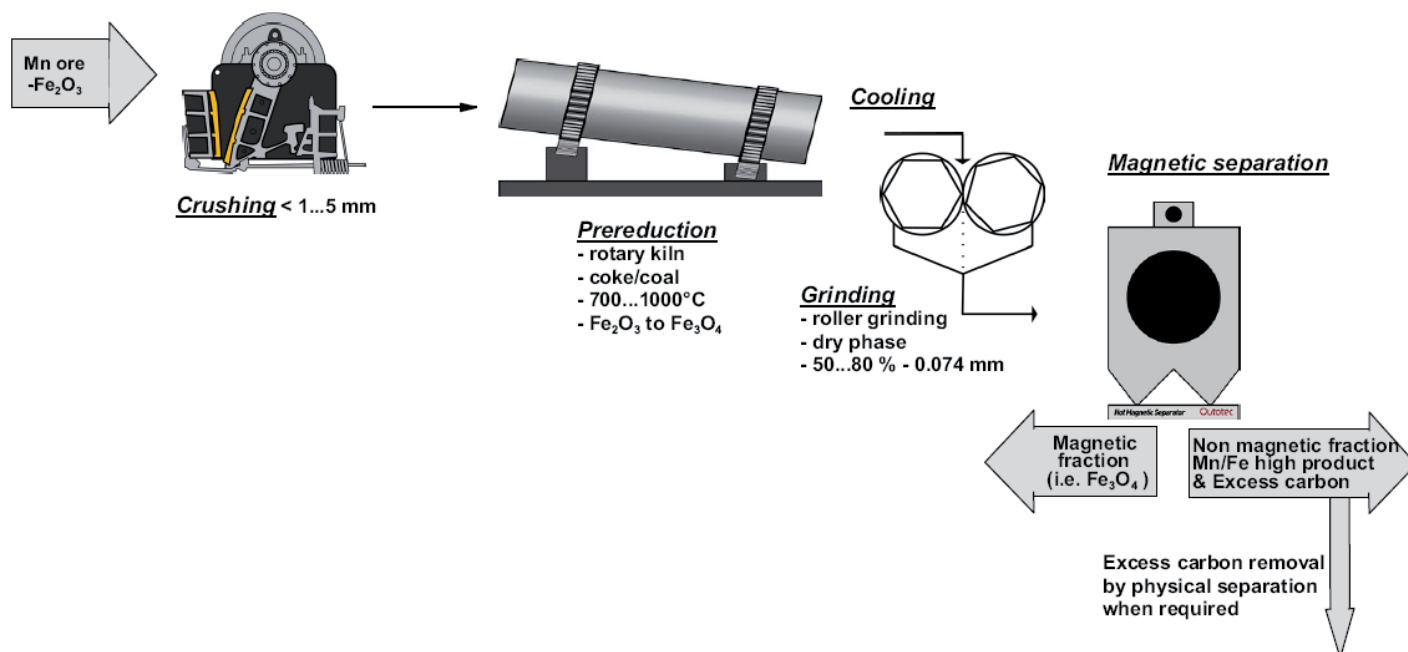


Figure 6: Suggested process flowsheet.

5 SUMMARY

Ore chemical analysis and structure:

The Mn/Fe ratio for grade A ore was 3.4 and for grade C ore was 1.9. Ore grade C contained more hydroxides and aluminium, which leads to a higher slag / metal ratio in the smelting phase. Both ores contained typical Mn compounds and the main phases were pyrolusite MnO_2 , cryptomelane $\text{KMn}^{4+}_6\text{Mn}^{2+}_2\text{O}_{16}$ and groutite $\text{MnO}(\text{OH})$. Iron was mainly in hematite and goethite form. Hematite and goethite grains were mainly disseminated in Mn phases and in various types of hydroxide precipitations. The size of these grains was 10 -100 μm .

Pre-reduction tests and magnetic separation:

A pre-reduction temperature of 1000°C resulted in an excessively low Mn/Fe-ratio of non-magnetic product. This was due to the fact that part of the iron was in metallic form but most of it was in non-magnetic Fe-Mn compounds. Metallic iron was in the form of fine disseminated grains, which are difficult to separate.

Results with a pre-reduction temperature of 800°C were very promising and, in magnetic separation, the non-magnetic fraction Mn / Fe ratio was 11-12, which is actually too high. In this case, Mn recovery was 65 % and mass fraction was about 55 %. In these values, carbon has been reduced.

The results allow an estimation that if the non-magnetic fraction Mn / Fe ratio is reduced to 8, then Mn recovery will increase to 75 %. Also in this case, Al_2O_3 -content is decreased from 9.6 %.

6 CONCLUSIONS

According to the tests shown in this paper, with controlled pre-reduction iron can be pre-reduced to magnetite form. Pre-reduced iron can be separated after grinding with magnetic separation.

High oxygen manganese phases will be reduced to low oxygen manganese phases in the pre-reduction. This low oxygen Mn phases will be re-oxides in the subsequent sintering stage. Iron will be oxides from magnetite to hematite form in the sintering stage, giving energy to this process step.

The Mn-ore upgrading procedure described in this paper could provide an economic way to expand possible Mn ore reserves globally. So far there has been enough high-quality Mn ore available, but the amount of high-quality Mn ores will decline in the future, especially locally.

The final conclusion is that crushing, pre-reduction, magnetic separation leads to an up-graded Mn-ore, which is an excellent raw material for ferromanganese production after pelletizing and sintering.

7 REFERENCES

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