

Sintered Manganese Ore and Its Use in Ferromanganese Production

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ABSTRACT

An increasing proportion of fine ore and concentrate is being used in ferroalloy production. This has inspired studies to process these materials in a more economical, reliable and environmentally friendly way in the face of ever-toughening competition in the industry.

A process for sintering manganese ore was developed by Outokumpu with equipment proven in the sintering of chromite. In the process, manganese ore fines are micro-pelletised and/or nodulised, sintered on a steel belt and then crushed to the proper size. Special attention is paid to the chemistry and phenomena of the sintering process itself in order to reduce energy consumption and create a basis for optimal dimensioning of the furnace.

The essential feature of the process is, that in this kind of sintering machine, the gas flows and sintering conditions can be accurately controlled and thus high quality durable sinter is produced with low energy consumption. The machinery is compact and gas-tight to meet demanding environmental requirements. Investment costs remain moderate and production costs low.

In this paper the process is first described in brief. Then pilot tests with different types of manganese ores are discussed with the sintering properties of the ores and physical and chemical characteristics of the sinter produced. Finally, the advantages of using sinter and preheated charge in smelting are discussed.

1. INTRODUCTION

The Outokumpu steel belt pelletising-sintering process has already been in use on commercial scale for chromite for over ten years. At the moment it is in use at three plants, in Finland and South Africa, and two are under construction. The process consists of wet-grinding and filtering of chromite concentrate and coke fines, pelletising the filter cake with bentonite, and finally sintering the pellets into hard, fired pellets. The pellets are sintered in a new type of Outokumpu steel belt sintering furnace. The sintering furnace is a multi-compartment furnace through which the pellets are conveyed on a perforated steel belt. Solid fine coke in the feed pellets is the main external energy source in the furnace. Secondary cooling gases are circulated from the cooling compartments to the front-end compartments to utilize this energy. Gaseous fuel is used as a minor external energy source to control the temperature profile in the furnace.

The steel belt sintering furnace is also being used for sintering niobium concentrate.

Outokumpu has developed this sintering process further for fine manganese ore using a furnace modified from the chromite application. The Outokumpu manganese sintering process and the research work done as the basis for the process are described in this paper. The benefits of using sinter are estimated at the end of the paper based on research work, theoretical calculations and on the experience from ferrochrome production.

2. OUTOKUMPU TYPE SINTERING PROCESS FOR MANGANESE FINES

The main process chart is typical for the sintering processes. Raw materials, such as fine manganese ore, return dusts, bentonite, coke fines, etc. are dosed and blended in a balling drum to form damp nodules or micro pellets for the sintering furnace.

The material is fed to the furnace by a shuttle feeder system to form a level bed on the steel belt. Screened sinter pebbles are fed first on the bottom of the bed as hearth layer. Additional fine coke is fed on the surface of the bed, Figure 1.

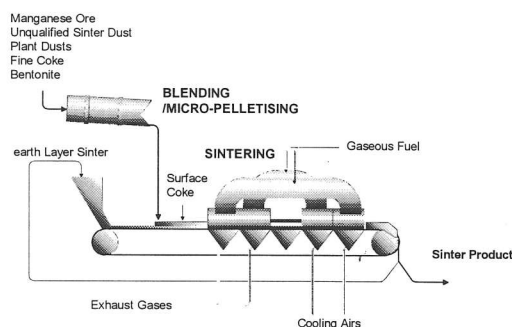


Figure 1 Outokumpu sintering process

The furnace consists of two front-end compartments, one for drying and one for sintering, and two cooling compartments. Hot gas is sucked through the bed from the bottom of the drying zone to dry the material. Hot gas to drying is conducted from the secondary cooling compartment. In the sintering zone hot gas is sucked in a similar way to heat the bed and ignite the coke. Reactions go through the bed as the belt moves forward. The gas to sintering is circulated from the first cooling compartment and the gas is further heated by gas burners, if required. This saves energy in the furnace. The hot gas coming to the bed maintains the temperature of the bed high throughout the whole zone. This increases the retention time at the reaction temperature and is essential for the quality of the product. The surface coke maintains the surface temperature high and decreases the amount of unsintered product.

The product from the furnace is crushed and screened. Fine material is returned for blending and sized material is circulated back to the hearth layer.

3. RESEARCH ON SOME MANGANESE ORES AND SINTERS

Outokumpu has made studies and manganese ore sinterings on pilot scale by its research center Outokumpu Research Oy in Pori. The study work and results from some batch sintering tests have already been described in the previous Infacon 8 in Beijing [1]. Further research is described here.

The batch sintering reactor and the continuous sintering machine located in the pilot plant were used. The chemical and physical properties of the sinters were determined in the Outokumpu Research laboratory.

3.1 Manganese ores used in pilot sintering

There are different types of manganese ore, for example hydroxide types and carbonate types. In this research two typical types of manganese ore have been used. Type 1 is a carbonate ore, of which the main carbonate is calcium carbonate. Type 2 has manganese oxides which oxidation degree is high. The main components and volatiles of the two ores are presented in Table 1. The volatiles in the analyses include also oxygen from the decomposition of MnO_2 to Mn_2O_3 .

The chemical analyses of feed materials and sinter products were analysed by wet chemical methods, using FAAS (flame atom adsorption spectrometer), ICP (plasma emission spectrometer) and Leco analysers.

Table 1 Chemical analyses of manganese ores in dry basis

	Type 1 [wt%]	Type 2 [wt%]
Mn	37	51
Fe	4.9	1.8
Fe 2^+	0.35	0.13
SiO ₂	6.0	2.7
MgO	3.9	0.07
CaO	12	0.07
Al ₂ O ₃	0.2	5
H ₂ O _{crystal}	1	5
CO ₂	16	-
volatiles	17	15

3.2 Pilot scale batch sintering reactor

The manganese ore agglomerates were sintered in a batch sintering system, Figure 2. The batch sintering system consists of a butane burner, a combustion chamber, a sintering reactor and gas lines. The gas lines are equipped with valves for feeding the combustion gas to the reactor and off-gas to the gas cleaning system. The sintering system is controlled continuously by an automatic control system. The positions of the thermocouples installed inside the agglomerated bed to measure the temperature during the sintering process can be seen in Figure 2.

Agglomeration was carried out on a disc with a diameter of 2.0 metres and a depth of 0.3 metres. The maximum rotation speed of the disc was 20 rpm. The manganese ore fines were mixed with fine coke in 20 kg batches using a horizontal mixer. The batch was fed manually onto the disc. It was moistened by water sprayers according to the formation of the agglomerates. The rotation speed and the inclination of the disc were adjusted according to the formation of the agglomerates. The green agglomerates were charged into the batch reactor without any separate drying.

Butane was burnt with air or with oxygen enrichment, depending on the process stage, to produce hot gas for the process. The hot gas

simulates the circulated gas in the full scale sintering machine. The normal batch sintering process comprises the following stages: drying with combustion gas, sintering with combustion gas using oxygen enrichment, and cooling with air.

For each zone, the amount of gas and the retention time were pre-selected. The combustion gas and cooling air were introduced into the reactor from above, but on a commercial scale cooling air would be fed from beneath. Moist agglomerates were charged into the reactor on a protective hearth layer. The height of both layers was about 200 mm. The surface coke above the agglomerated bed was 20 mm deep.

3.3 Pilot scale continuous sintering equipment

A schematic drawing of the pilot scale continuous sintering machine is presented in Figure 3. The specific values of this continuous sintering machine are:

- thick perforated belt made of steel, and edges made of steel and brick
- effective length 6.1 m
- effective width 200 mm
- belt speed 50 - 200 mm/min
- total bed height 450 mm
- butane gas used as fuel

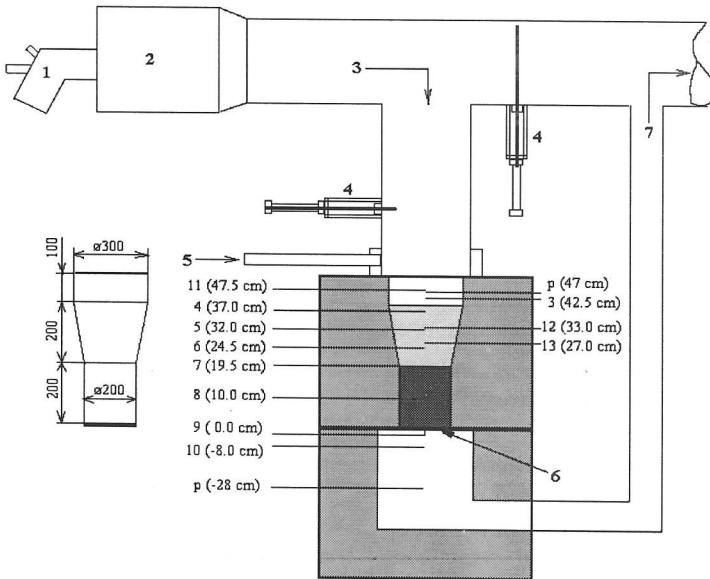


Figure 2 Pilot scale batch sintering equipment

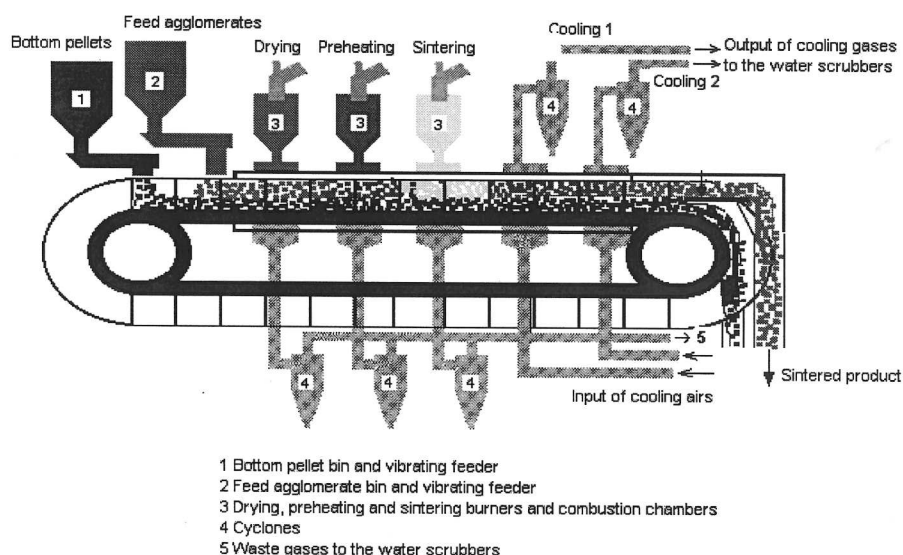


Figure 3 Pilot scale continuous sintering machine

The continuous sintering system consists of the sintering machine, feeding equipment, butane gas burners with combustion chambers for each reaction zone, and cleaning systems for off-gases.

The sintering system was originally divided into 5 zones:

1. Drying zone (residual moisture)
2. Preheating zone
3. Sintering zone
4. Cooling zone 1
5. Cooling zone 2

In the case of sintering manganese agglomerates the drying and preheating zones were combined, and only one zone was used during the test procedure.

Each zone is furnished with a refractory lined chamber. The temperature and pressure of each zone can be controlled individually. For the first three reaction zones the combustion gases are blown from above. Combustion gases consist of butane, air, and possible oxygen enrichment. In this case the first zone was not used. For the cooling zones air is blown from beneath through the pellet or sinter layers.

The agglomerates made of manganese ore fines were fed from the agglomeration disc directly by belt conveyor onto the bottom pellets. Sintered chromite pellets are used as bottom pellets in this scale. The total height of the bed was adjusted to 420 - 450 mm, which was controlled by the feed amount of the agglomerates or that of the feed mixture onto the disc. The surface coke was fed onto the bed just after the feed point of the agglomerates and its thickness was 5 - 10 mm. Coke was charged from a small silo by a small vibrating feeder. In the tests the fixed carbon in the bed was 5.5 wt-% and on the surface 2.4 wt-%, in total 7.9 wt-%.

Temperatures were measured by thermocouples. They are located in each reaction chamber, just above the pellet bed. Gas line temperatures were measured directly from the gas stream.

3.4 Temperature profiles of sintering

The continuous sintering process is controlled by controlling the temperature profile in the furnace. The temperature profiles through the bed itself during the process can be measured only in the batch sintering reactor. They give the basis for studying the reactions in each process phase and

further for process calculations and dimensioning of the furnace.

The thermocouples in the batch reactor were located inside the agglomerated fresh charge, in the bottom layer and in the gas phase above the charge:

- Nos. 3 and 11 in the gas phase
- No. 4 in the upper part of the fresh bed (close to the surface of the bed)
- Nos. 5 and 12 in the middle of the fresh bed
- Nos. 13 and 6 in the lower part of the fresh bed

The gas phase temperature demonstrates the gases transported from the cooling zones to heat the batch. From the latest cooling zone, where the temperature is low, the gases are led to the drying zone where excess temperature has a negative effect. From the first cooling zone, where the gases are hot, the gases are led to sintering zone to promote sintering. The other source of energy is coke mixed into agglomerates. The amount of coke mixed in the batch sintering charge of Type 1 ore was 4.0 wt-% (fixed carbon) and additional coke on the surface 3.0 wt-%, in total 7.0 wt-%. The coke amount mixed to the batch sintering charge of Type 2 ore was 4.3 wt-% (fixed carbon) and additional coke on the surface 4.3 wt-%, in total 9.6 wt-%.

In the drying zone the moisture in the agglomerates will be dried out. The retention time in the drying zone for Type 1 ore was 6.0 min. The maximum temperature of the feed gas was 360°C, Figure 4.

The retention time in sintering was 7.0 min. The surface temperature of the fresh bed followed the temperature of feed gas very accurately. The maximum temperature of the feed gas was 1100°C depending on the amount of butane. The peak temperature of the surface of the bed was as high as 1500°C because of the use of surface coke. The surface coke burned very rapidly. The temperature in the middle layer of the fresh bed was 1380°C, and the maximum temperature of the lower layer was 1400°C.

For Type 2 ore the retention time in the drying zone was 8.0 min. The maximum temperature of the feed gas in drying was 480°C. The agglomerate layers dried from the top layer towards the bottom during the drying period, Figure 5.

The retention time in sintering was 7.0 min as for Type 1 ore. The maximum temperature of the feed gas was 1020°C (thermocouple 11). The maximum surface temperatures of the bed (thermocouple 4) was 1440°C. The higher the temperature of the feed gas the higher surface temperature was achieved. The surface coke provided energy only for the upper part of the bed and thus eliminated the unsintered material. The maximum temperatures in the middle layer were 1520°C and in the lower layer 1530°C.

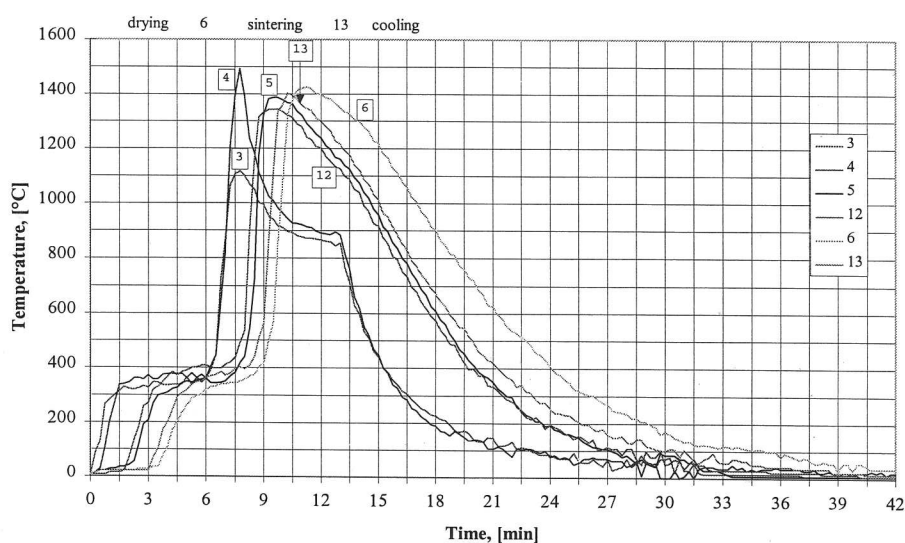


Figure 4 Temperature profiles of batch sintering test of Type 1 manganese ore

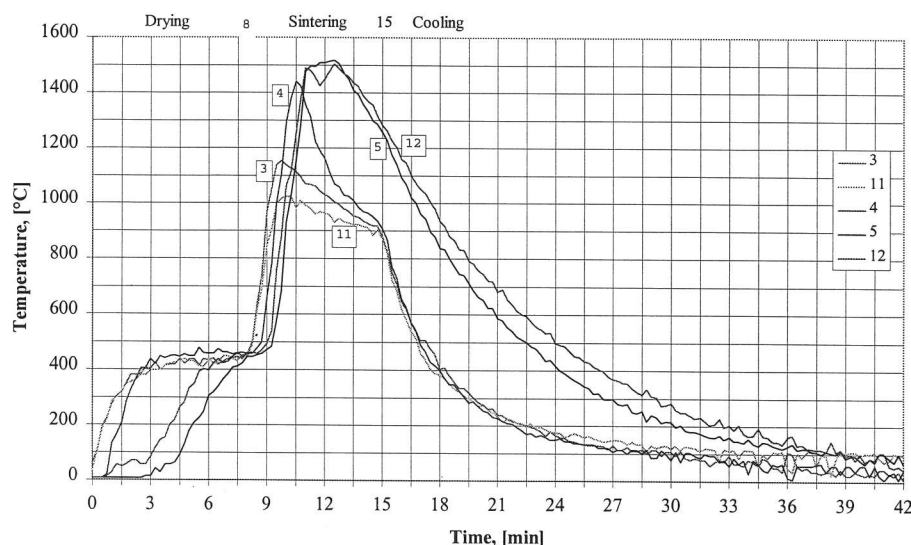


Figure 5 Temperature profiles of batch sintering test of Type 2 manganese ore

The cooling rate of the manganese ore sinter was slower than that of, for example, chromite pellets. The sinter contains plenty of pores, but individual pellets cool down more effectively than sinter. The cooling air may channel more in a sinter bed than in a pellet bed and thus the cooling time is a little longer. Thus the cooling time is relatively long and a large volume of cooling air is needed. Attention should be paid to the distribution of the cooling air.

3.5 Thermogravimetric analysis of manganese ores

For further studying the reactions in different temperature zones thermogravimetric analyses were made for the ores both in oxidising and reducing conditions.

Thermogravimetric analyses have been made with Netsch STA 409 equipment. The temperature increase and decrease rate was 5°C/min. The peak temperature in oxidizing conditions was 1050°C, and the peak was reached two times. The temperature decreased to 200°C between the peaks. In reducing conditions the highest temperature was 1500°C. The amount of gas into

the furnace was 100 cm³/min. Test samples weighed about 30 mg each.

During the first temperature increase period volatilising components leave the sample, and the weight falls considerably. Type 1 is a carbonate ore. For example calcium carbonates decompose to calcium oxide and carbon dioxide gas. Manganese oxides have a high oxidation degree in Type 2 ore. These manganese oxides (MnO₂) decompose to a lower oxidation degree during the first heating period, and the weight goes down. This is an irreversible reaction. (Figures 6 and 7)

In an oxidizing atmosphere the oxidation degree of manganese oxide decreases to Mn₃O₄ during heating and shoot up drastically back to Mn₂O₃ during cooling with both, Type 1 and Type 2 ores. Therefore this is a reversible reaction. The reversibility depends on the partial pressure of oxygen. For Type 1 ore with air atmosphere it is not possible to see any reversibility, and for Type 2 ore it is possible to see some slight reversibility. (Figures 6 and 7)

Carbon monoxide gas reduces manganese oxides efficiently. There could also be some carbide formation with the use of carbon monoxide gas.

Coke also reduces manganese oxides despite the oxidizing conditions with air. (Figures 8 and 9)

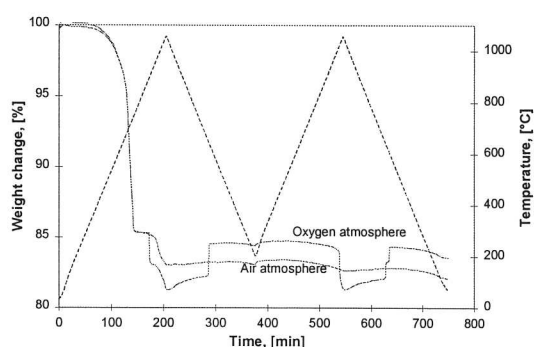


Figure 6 Thermogravimetric analysis of Type 1 manganese ores, oxidizing conditions

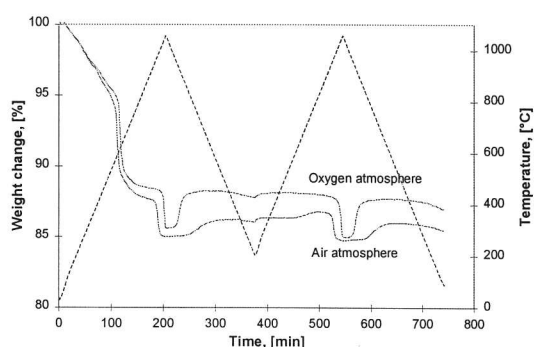


Figure 7 Thermogravimetric analysis of Type 2 manganese ores, oxidizing conditions

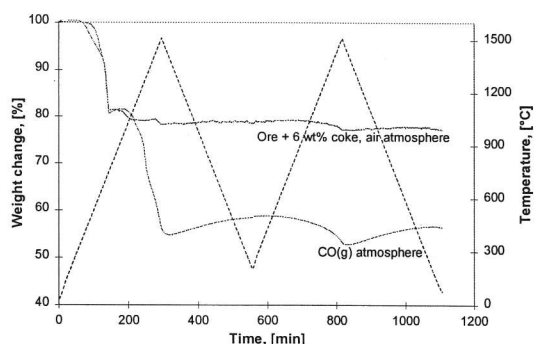


Figure 8 Thermogravimetric analysis of Type 1 manganese ores, reducing conditions

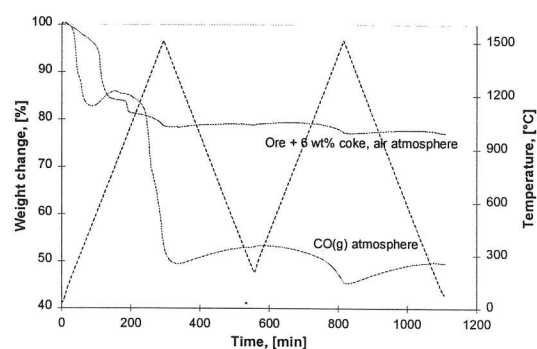


Figure 9 Thermogravimetric analysis of Type 2 manganese ores, reducing conditions

3.6 Chemical analyses of sinters

The chemical analyses of the sinters are presented in Table 2. Different oxide components for determining the reduction level of manganese oxides in the sinters were analysed. The manganese content is about 18 and 21 wt% higher in sinters than in ores because the volatile components disappear from ores during sintering. Type 1 sinter contains in addition iron oxides, silica, magnesia and calcium oxide. Type 2 sinter contains aluminium oxide, and some iron oxides and silica.

Table 2 Chemical analyses of sinters

	Type 1 [wt%]	Type 2 [wt%]
Mn	45	60
Fe	5.9	3.3
SiO ₂	8.6	3.7
MgO	5.0	0.42
CaO	14.4	1.6
Al ₂ O ₃	0.73	5.9
K ₂ O	0.006	0.67
P ₂ O ₅	0.03	0.18

The reduction levels of manganese sinters in tests of Type 2 ore were calculated based on the amount of pure manganese and the amounts of all oxides of the sinter other than manganese oxide. The oxidation degree of manganese oxides is difficult to measure directly. Therefore the reduction level of manganese oxides is calculated, and the results are presented in Table 3.

Table 3 Reduction levels of manganese oxides of Type 2 sinters

	Type 2
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O/Mn-mole ratio	1.26
MnO [wt%]	29.5
Mn ₂ O ₃ [wt%]	70.5
MnO/Mn ₂ O ₃ [wt%]	0.42
Mn ²⁺ / Mn _{tot} [wt%]	31.7

3.7 Microstructure of sinters

The microstructure of sinter products were studied by X-ray diffractometry (Type D 500, Siemens), a scanning electron microscope (Cambridge SEM 360) and a light microscope.

In Type 2 sinters which were made by batch sintering, the sinter pieces contained many pores and thin cracks. The macropores were formed during the sintering process when the gases flowed through the partly molten bed and the micropores correspondingly when the volatiles decomposed. The cracks were formed mainly during cooling.

The manganese oxide phases were mainly manganosite, hausmannite and galaxite. Manganese oxide (Mn₃O₄) was also identified according to X-ray diffraction.

The structure grains were sintered by silicate bonds which were Ca,Mn-silicates. The main silicate appeared as johannsenite. Glaucochroite, (Ca,Mn)₂SiO₄, was also detected. The silicate phases appeared as dark areas in the microscopic pictures and the manganese oxides as light grey areas, Figure 10.

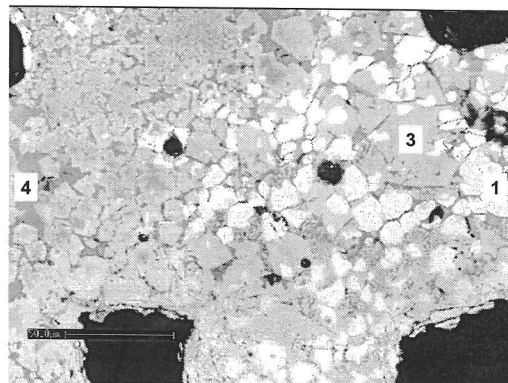


Figure 10 Microstructure of Type 2 sinters, batch sintering (magnification 500 times)
1. Manganosite 3. Galaxite 4. Johannsenite Black areas: Pores

In Type 1 sinters (Figure 11) made by continuous sintering, the microstructure of the sinters contained different manganese oxides. The manganese oxide grains were sintered by silicate bonds. Manganese sinter typically contained three different morphological microstructures:

- manganese oxides grains were large and angular due to long enough time to grow from

the melt during crystallization in the first cooling zone

- small spherical and elliptical manganese oxide grains
- silicate phase also contained manganese and formed bonds

During decomposition of the volatiles and the burning of carbon, a large degree of microporosity and macroporosity in the microstructure was formed. The macroporosity was also formed due to the gas flow through the partly molten bed. The distribution of pore sizes was quite large.

The main phases of the sinters according to X-ray diffraction are presented in Table 4.

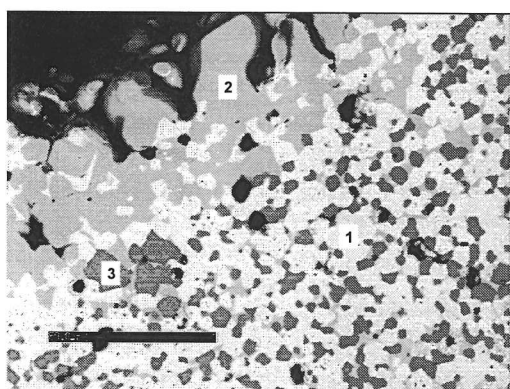


Figure 11 Microstructure of Type 1 sinters, continuous sintering (magnification 500 times)
1. Hausmannite 2. Calcium manganese oxide 3. Dicalcium silicate Black areas: Pores

Table 4 Main phases of the sinters

Phase	Type 1	Type 2
Manganosite, MnO	x	x
Manganese oxide, Mn ₂ O ₃	x	
Iwakite, MnFe ₂ O ₄	x	
Braunite, MnMn ₆ SiO ₁₂	x	
Merwinite, Ca ₃ Mg(SiO ₄) ₂	x	
Hausmannite, (Mn,Mg)(Mn,Fe) ₂ O ₄		x
Magnetite, FeFe ₂ O ₄		x
Manganese oxide, Mn ₃ O ₄		x
Hematite, Fe ₂ O ₃	x	x
Galaxite, MnAl ₂ O ₄		x

Diopside, Ca(Mg,Fe,Al)(Si,Al) ₂ O ₆		x
Johannsenite, CaMnSi ₂ O ₆		x

3.8 Physical properties of sinters

The abrasion test values give the trend for dust formation of the sinter during transportation and in the handling equipment, e.g. from the feeding system to the smelter and inside the furnace.

Abrasion resistance of the sinter product was measured using the modified Tumbler method. The batch consisted of a sample of 1 kg. The sinter was crushed and screened to a grain size of 5 - 25 mm. This test was performed in a steel drum (D = 180 mm, L = 200 mm). The rotation speed was 23 rpm. Each test comprised three rotation periods: 8 min, 24 min, 58 min (total times 8, 32, 90 min, respectively). After each period the entire batch was screened with sieves of 0.59 mm and 5.0 mm. After screening the batch was returned to the drum and the test was continued. The screen analyses obtained describe the fines formation and are presented as a function of rotating time.

The abrasion resistance is a little better in sinters made with the pilot scale continuous sintering equipment compared to batch tests. But the difference between them is not significant. There are no differences of abrasion resistances between batch sinters, Figure 12.

The formation of coarse dust, below 5.0 mm, was a little smaller from the Type 2 ore sinters, especially during a long period rotating time. In pilot scale continuously made sinters the quality was also good, Figure 13. The crushed sinter contained many edges, and that could easily generate dust in drumming.

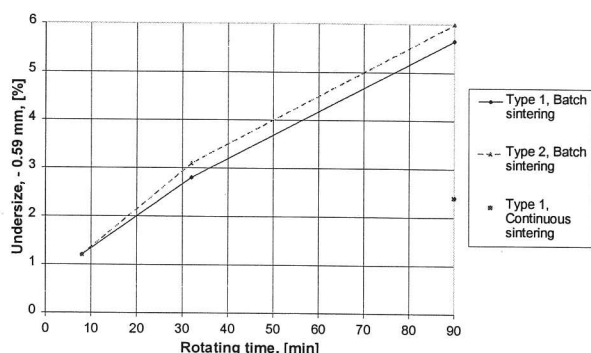


Figure 12 Abrasion indices of sinters as function of rotation time, sieve 0.59 mm

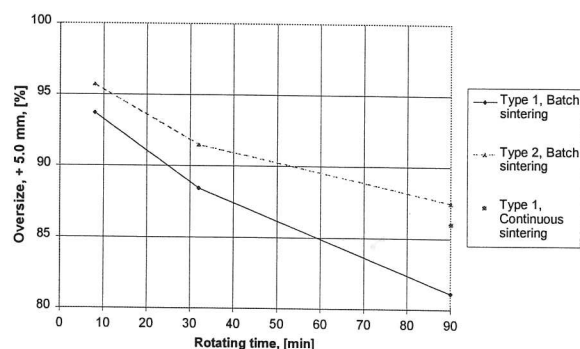


Figure 13 Tumbler indices of sinters as function of rotation time, sieve 5.0 mm

4. FIGURES FOR COMMERCIAL SCALE

The following figures are estimated as consumption figures for commercial scale of sintering furnace. The estimates are based on the pilot scale test runs with manganese fines and on Outokumpu's experience on pilot scale runs and commercial operation with chromite concentrate and niobium concentrate.

Consumption figures:

Solid fuel as fixed carbon at the range of 5-6 %, i.e. 540 kWh/t.

This is about 6-7 % as coke.

Gaseous fuel (e.g. CO-gas) at the range of 30 kWh/t

Electricity, at the range of 20 kWh/t

The product quality is estimated to be more homogenous compared to conventional grate sintering process due to high sintering gas temperature and use of surface coke. This means decreased amount of unqualified sinter which is returned back to the process.

The typical capacity area for the Outokumpu manganese sintering process is from 100,000 tpa to 700,000 tpa. Because of light belt construction the process is economical also in the small capacity range.

5. ADVANTAGES OF USING SINTER IN SMELTING

The following advantages of sintering and the use of sinter in blast furnaces and electric furnaces are commonly known: [2, p.509]

- Fine ore, which has a limited application and value in conventional smelting is agglomerated and converted to a superior product
- Reduced gas volumes, and hence fewer furnace eruptions, result when smelting sinter
- Furnace availability and operating loads are increased
- Better porosity of the burden with easier penetration and elimination of the gas generated by the reduction reactions

In addition to listed, due to the characteristics of the product sinter, the smelting furnace can be equipped with preheating. The same type of preheating shaft kiln as used in Outokumpu's ferrochrome process, can be used for preheating of ferromanganese feed batch. The preheating kiln is a stationary shaft kiln where the smelting charge is preheated by hot combustion gas in non-oxidising conditions in a counter current method. The charge material can be heated up to 400 – 500 °C. The heated material flows by gravity through the charging tubes to the smelting furnace. CO-gas from smelting is utilised in the process.

In conventional smelting, the ore typically contains MnO₂. The reaction with carbon is exothermic causing eruptions in smelting furnace when the fines block the burden. In preheating the ore the reaction increases the temperature uncontrolled in the kiln. This normally limits the preheating of ore only to drying. The properties of manganese sinter are different as described above. In sinter the manganese oxides are already reduced to lower oxidation level. This means that the sinter can be heated with coke in the charge. The limitations come from Boudouard reactions ($C + CO_2 = 2CO$) when heating of coke up to and over 700 °C.

For the same reason the furnace can be closed, which allows the utilization of furnace gas rich in carbon monoxide (CO). The furnace gas is scrubbed and CO-gas is utilised as fuel in preheating kiln and sintering furnace.

Usage of sinter and also related utilization of preheating gives major advantages for the smelting process:

The specific energy consumption in smelting with lumpy ore and sinter is typically in the range of 2,200 – 3,000 kWh/t of HCF₂Mn [2, p.531]. When preheating the furnace charge the savings in electric energy consumption in smelting is about

300 kWh/t of smelted metal, which is directly related to increased production.

The energy content of CO-gas from smelting is about 1,500 kWh/t of liquid HCF₂Mn. This can as high as by 80 – 100 % be utilised in the pre-processes or elsewhere in the plant.

6. CONCLUSION

Outokumpu has made extensive research on sintering of manganese fines among the other materials. The test runs with batch sintering equipment and especially with pilot scale continuous sintering machine prove clearly that it is possible to make good quality manganese sinter with Outokumpu sintering process. The Outokumpu's experience on pelletising of chromite concentrate gives the background for scale up the process from pilot runs to operational scale. It gives also the strong belief on the thought of sinter as superior quality feed material to the smelting furnace. Outokumpu has three decades experience on the advantages of chromite pellets in smelting and the same advantages have been reported by numerous ferromanganese producers.

Outokumpu's manganese sintering process is energy saving reliable process, which is economical also in smaller scale. The use of sinter is advantageous in smelting itself. With use of sinter the furnace can also be closed, furnace CO-gas can be utilized and the feed can be preheated. This all results in smaller consumption figures and finally in increased production.

7. REFERENCES

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