The Application of Steel Belt Technology for the Sintering of Manganese Ore Fines

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Abstract

Outokumpu has made extensive studies on different agglomeration methods in order to find the most economic, reliable and environmentally friendly concept for the production of ferrochrome from the fine concentrate made from low grade ore.

On the basis of these studies the pelletising and steel belt sintering process was selected as the new pretreatment method of furnace feed at the Ferrochrome works in Tornio.

With the equipment proven in the sintering of chromite and experience and knowledge accumulated in the course of development work the idea of also using steel belt technology for the sintering of manganese fines was found interesting. The use and advantages of good quality manganese sinter is well known in the production of ferromanganese.

The essential feature of the process is that in this kind of sintering machine, the gas flows and sintering conditions can be accurately controlled. Thus high quality durable sinter is produced with low energy consumption. The machine is made very compact and gas tight and thus the investment costs remain moderate, production costs low and even strict environmental requirements are met.

In this paper the process and related phenomena, the main mineralogical changes in manganese ore and their effects on further processing of the material as well as the advantages achieved are described. Consumption figures typical for the intering and subsequent smelting process are also given in the form of example calculations.

Introduction

Outokumpu started ferrochromium production in Finland in 1968. The ferrochromium plant was built close to chromite deposits. The Kemi Mine contains low grade chromite and its Cr/Fe-ratio is 1.5 - 1.6.

The targets of the ferrochromium process were low electric energy consumption in smelting, high on-line availability, good working conditions and sound environmental aspects.

The ferrochrome process consists of the pelletising and sintering of ground chromite, preheating and smelting the charge.

The sintered pellets and other charge components are preheated in a stationary shaft-type preheater. The furnace itself is a closed type and thus the furnace gas can be utilised for various purposes.

At the end of 1989, a new steel-belt sintering plant was started which operates efficiently and economically. The steel belt sintering furnace is a multi-compartment furnace through which the green (=new) pellets are carried on a perforated steel belt. The thermal energy required is obtained by combustion of coke dust added to the pellets and CO-gas from the electric furnace. Energy consumption is minimised by re-circulating exhaust gases from cooling.

The application of the steel belt sintering system seems very attractive for the sintering of manganese ore fines based on the laboratory and bench scale tests and the process calculations. The use of the sinter also allows the preheating of the charge, resulting in significant energy savings in smelting.

Background

General

Theoretical considerations in this presentation focus on MnO_2-containing manganese ore fines. This ore contains the following main phases:

- Pyrolysite (MnO_2)
- Vernadite (MnO_2*2H_2O)
- Gibbsite ($Al_2O_3*3H_2O$)
- Goethite ($Fe_2O_3*H_2O$)
- some SiO_2

The manganese hydroxide contains iron and aluminium. The gibbsite also contains iron. Potassium and barium appeared in the manganese hydroxides.

The basic idea of sintering is to focus the exothermic oxidation of carbon and the energy of the circulating hot process gases to particular stages of the process. In the steel belt sintering process, oxidation and reduction reactions occur simultaneously together with melting in layers throughout the bed. Solidification of melt phases occurs also in layers through the bed in the cooling zones.

The steel belt sintering furnace is divided into four zones. The first zone is the drying zone where secondary cooling gases (from the fourth zone) are used for partial removal of moisture and to preheat the wet feed to some extent. The second zone is the reaction zone, where carbon is ignited and a thin molten reaction layer moves horizontally downwards, producing hot porous sinter as the process gases go through the layer. The third zone begins when the reaction layers reach the end of the wet feed layer (see Fig. 1) and the primary sintering reactions are stopped. In the third zone (the first cooling zone), the hot solid porous sinter is cooled rapidly and hot process gas is conveyed to the reaction zone. In primary cooling, some reoxidation of iron and manganese occurs, increasing the temperature of the process gas. During the secondary and final cooling, reactions are negligible.

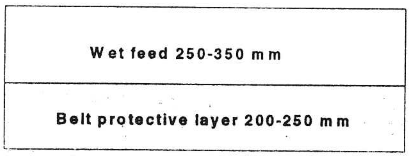

Fig. 1. Sintering furnace feed.

Mn-C-O stability diagrams

The stable crystaline phases of the Mn-O system are MnO_2, Mn_2O_3, Mn_3O_4 and MnO. In sintering, the temperature will rise to about 1350°C.

Fine coke and hot circulating gases are used as sources of energy. Fig. 2 and Fig. 3 present Mn-C-O phase diagrams at 1350°C and 800°C as a function of partial pressures O_2 and CO_2.

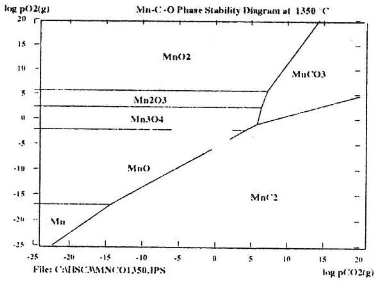

Fig. 2. Phase stability diagram of the Mn-C-O system at 1350°C.

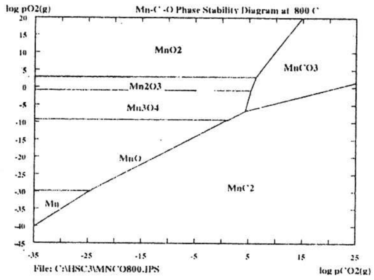

Fig. 3. Phase stability diagram of the Mn-C-O system at 800°C.

The shaded areas in Fig. 2 and 3 roughly indicate process conditions as a function of partial pressure of oxygen and carbon dioxide.

Main reactions

In sintering, many reactions take place in the bed between manganese oxides, iron oxides and carbon and air. Examples of the following main reactions are presented in this connection.
The main reactions for manganese oxides are:

$MnO_2=1/2Mn_2O_3+1/4O_2(g)$	$\Delta H^0_{298}=+41.5$ kJ	Eq. 1
$Mn_2O_3+1/6C=2/3Mn_3O_4+1/6CO_2(g)$	$\Delta H^0_{298}=-33.9$ kJ	Eq. 2
$Mn_3O_4+1/2C=3MnO+1/2CO_2(g)$	$\Delta H^0_{298}=+35.4$ kJ	Eq. 3
$MnO+1/6O_2(g)=1/3Mn_3O_4$	$\Delta H^0_{298}=-77.4$ kJ	Eq. 4
$Mn_3O_4+1/4O_2(g)=3/2Mn_2O_3$	$\Delta H^0_{298}=-47.5$ kJ	Eq. 5

The free oxygen of equation 1 reacts very strongly with carbon and/or CO inside the bed. The Boudouard-reaction also occurs, $CO_2+C = 2CO$.

Hydrates decompose according to the following reactions:

MnO2*2H2O=MnO2+2H2O(g)	$\Delta H^0_{298}=$ not known	Eq. 6
Al2O3*3H2O=Al2O3+3H2O(g)	$\Delta H^0_{298}=+185.8$ KJ	Eq. 7
Fe2O3*H2O=Fe2O3+H2O(g)	$\Delta H^0_{298}=+51.9$ KJ	Eq. 8

Manganese oxide reacts with alumina and silica forming manganese aluminate and silicate. These oxides contain various amounts of iron and other components replacing manganese oxide in the lattice.

MnO+Al2O3=MnO*Al2O3	$\Delta H^0_{298}=-39.9$ kJ	Eq. 9
2MnO+SiO2=2MnO*SiO2	$\Delta H^0_{298}=-44.02$ kJ	Eq. 10

Iron reacts in sintering mainly according to the following reactions:

$Fe_2O3*H_2O= Fe_2O_3 +H_2O(g)$	$\Delta H^0_{298}=+51.9$ kJ	Eq. 11
$Fe_2O_3+1/6C=2/3Fe_3O_4+1/6CO_2(g)$	$\Delta H^0_{298}=+13.1$ kJ	Eq. 12

$FeO+1/2C=Fe+1/2CO_2(g)$ $\Delta H^0_{298}= +75.3$ kJ Eq. 13

$Fe+1/2O_2(g)=FeO$ $\Delta H^0_{298}= -272.0$ kJ Eq. 14

$FeO+1/6O_2(g)=1/3Fe_3O_4$ $\Delta H^0_{298}= -100.8$ kJ Eq. 15

Results on bench scale

The sintering tests of the manganese ore fines were performed on bench scale in a batch sintering reactor to clarify the process parameters of sintering for a commercial scale.

Performance of the batch sintering tests

The batch sintering system consisted of a butane burner, a combustion chamber, reactor and gas lines. The gas lines were equipped with the necessary water-cooled valves for leading the combustion gases to the reactor and off-gases to the gas cleaning system. The sintering process was controlled continuously by an automatic process control system.

The outer diameter of the reactor was 1.0 m and the height was 1.4 m. The reactor was lined with refractory and insulation castable mixes. Several thermocouples were installed inside the bed to measure the prevailing temperatures during the sintering process. The inside diameter of the reactor and the positions of the thermocouples can be seen in Fig. 4

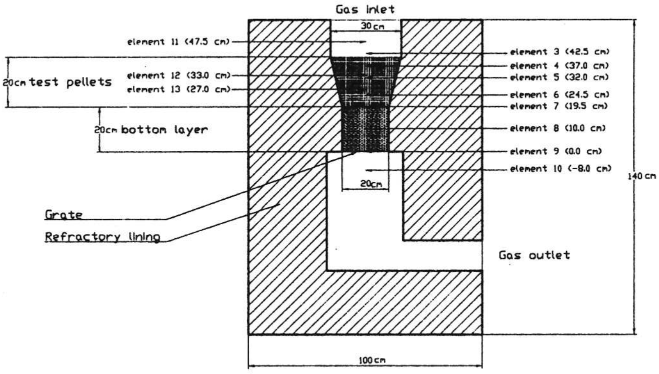

Fig. 4. Schematic drawing of the batch sintering system.

Butane gas was burned with air or with an oxygen enrichment, depending on the process stage. Oxygen enrichment was used due to the small scale.

The batch sintering process comprised the following stages:

- drying with combustion gases
- preheating with combustion gases using an oxygen enrichment
- sintering with combustion gases using an oxygen enrichment
- cooling with air.

For each zone, the gas amount and the retention time was preselected. The temperature of the combustion gases were conveyed by the amount of butane, air ratio and oxygen enrichment. The combustion gases were conveyed to the reactor from above. Cooling air was conveyed to the reactor from above, but on a commercial scale these gases were introduced from beneath.
Moist micropellets were charged into the reactor on the bottom layer (the protective layer). The height of the bottom layer was 200 mm and that of the micropelletised feed 200 - 250 mm. The weight of the moist micropelletised feed was 15 - 18 kg.

The sintered pellets were discharged from the reactor after the programme was finished and the batch was cooled to below 100°C

The batch was cooled to below 100°C and the sinter was discharged. The sinter was divided mostly into two sections (the upper and lower part) for analysing and for visual observations. The bottom layer was changed after every test.

Results

Raw materials

The main phases of the manganese ore fines were as earlier explained.

The chemical analyses of manganese ore fines are presented in Table 1 and the screen analyses of manganese ore fines in Table 2.

Table 1. Chemical analysis of manganese ore fines

Mn_{tot}	Fe_{tot}	SiO_2	Al_2O_3	MgO	CaO
41.9	5.2	4.0	13.3	0.3	0.1

K	Ba	S	P	CO_2	H_2O
0.8	0.3	0.01	0.032	0.1	7.2

Table 2. Screen size analysis of manganese ore fines.

mm	Undersize, %
10.0	100
6.7	96
3.4	71
1,7	45
0.8	29
0.2	15
0.074	9
0.037	6

Fine coke was used as a fuel in the bed in these tests.

Heating test in an N_2-atmosphere

The heating tests of very fine manganese ore were performed by DTA/DGA in an N_2 atmosphere and the following endothermic reactions were detected up to 800°C:
- 282°C: decomposition of gibbsite and goethite
- 510°C: decomposition of pyrolysite and verdandite to Mn_2O_3
- 725°C: decomposition of Mn_2O_3 to Mn_3O_4.

The weight loss of the sample mainly took place up to 800°C but the thermic reduction of Mn-oxides continued at higher temperatures.

Heating tests in a coke bed

The mixture consisted of manganese ore fines (-1 mm) and fine coke (-1 mm) which were briquetted. The mixture contained 18 % coke and 82 % manganese ore. The C_{fix} of coke was 81.7 %. The heating tests were performed in a tube furnace at the different temperatures. The N_2 gas was blown into the furnace during the rewts. The batch was cooled down by a large amount of N_2. The phase transformations of the product were detected according to the X-ray diffraction. The results are presented in Table 3.

Table 3 Phase transformation of manganese ore with coke at different temperatures

Temperature, °C	Weight loss, %	Phases	Comments
25		MnO_2, $Mn(OH)_4$, $Al(OH)_3$, (Mn,Al)-hydrated silicate, FeOOH, SiO_2	
500	11	$MnO_{1.88}$, Mn_2O_3, C	decomposition of hydroxides, almost the same structure as the original sample
800	19	Mn_3O_4, $MnAl_2O_4$, C	reduction of manganese oxides, formation of Mn-aluminate
1000	22	MnO, $MnAl_2O_4$, α-Fe, C	reduction of Mn-oxides, finely dispersed metallic iron
1200	31	MnO, $MnAl_2O_4$, Mn_2SiO_4, α-Fe-Mn, Mn-carbide, C	formation of Mn-silicates, metallic/carbide brills; grain size 1 - 50 μm
1300	34	MnO, $MnAl_2O_4$, Mn_2SiO_4, α-Fe-Mn, Mn-carbide, C	melted sample, formation of large metallic/carbide brills; grain size up to 2 mm

The manganese ore reduced strongly in a coke bed at high temperatures, ie over 1000°C. It was observed that the sample melted at 1300°C. These results give guidelines for the sintering conditions although on a commercial scale the coke amount is smaller and the gas atmosphere is slightly different. It can be assumed that in sintering the decomposition reactions and reduction of Mn-oxides occur at slightly lower temperatures when a large amount of gas is used.

Micropelletising of manganese ore fines

A bentonite was used as a binding agent in pelletising. The coke amount varied from 3 to 7 w-% of the ore amount. The batch pelletising tests were carried out on a disc with a diameter of 2.0 m and a depth of 0.3 m. The maximum rotation speed was 20 rpm.

The manganese ore fines were mixed with bentonite and fine coke in 30 kg batches using a horizontal mixer.

The micropelletising of the ore fines was easy to perform but the dried strength of the micropellets was too low without the bentonite. The moisture content of the micropellets was about 16 %. The manganese ore fines had a porous structure, sucking water easily into the grains. The grain size of the dry micropellets, which contained 7 w-% fine coke and 1 w-% bentonite, is presented in Table 1.

Table 4. Grain size of the dry micropellets

mm	Undersize %
9.52	100
4.76	78
3.36	50
1.68	13

The addition of bentonite clearly decreased the amount of fine fraction of the micropelletised product. The grain size of the micropellets was not coarser when the ore fines were pre-crushed to below 1.19 mm.

The fine fraction of the manganese ore fines is micropelletised by itself and/or by sticking to the surface of coarse grains.

Sintering of micropelletised manganese ore

Microstructure of the sinter product

According to X-ray diffraction the main phases of the product were as follows:

- Mn_3O_4, manganese oxide
- Mn_2AlO_4, manganese aluminium oxide
- MnO, manganosite
- Mn_2SiO_4, tephroite

The microstructure of a typical sinter is presented in Fig. 5.

Manganese appeared in manganese oxides and in different kinds of Al-oxides, which contained iron. The binding phases were mainly manganese silicates which also contained potassium.

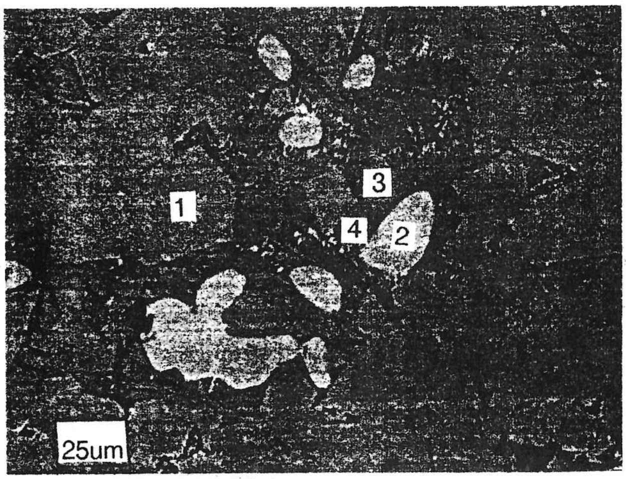

Fig. 5. The microstructure of the sinter. 1 = Mn-aluminate, rich in iron; 2 = Mn-oxide; 3 = Mn silicate, which contains Al, Ti, Fe, K and Ca; 4 = Mn-silicate, rich in potassium

Abrasion resistance of sinter

The sinter product contained only a small amount of unreacted or loose ore fines and was below 2 % of the total product. On this scale the wall and surface effects easily caused a thin unreacted layer on the walls of the reactor.

A small amount of coke was added to the surface of the bed to eliminate the unreacted layer.

The product was crushed to a grain size of 10 - 40 mm for the abrasion tests.

The abrasion tests were carried out in a steel drum 180 mm in diameter and 200 mm in length, which was equipped with lifters. The batch consisted of a sample of 1 kg. The rotation speed was 23 rpm. Each test comprised two different rotating periods: 8 min and 90 min. After each period the whole product was screened with sieves of 4.76 and 0.59 mm. Screen analyses which describe fines formation were obtained as a function of the rotation time. The crushed and screened product was not pre-drummed before the tests.

The results of the sinter sample are shown in Table 5.

Table 5. Abrasion test results

Rotation time, min	Undersize, %	
	4.76 mm	0.59 mm
8	5	2
90	17	9

The fines formation of the product sinter in these tests was small. The amount of fines below 0.59 mm was even lower than that of the good quality chromite sintered pellets. Thus the fines formation in the dosing, preheating and on the surface of the bed in the electric furnace will be very low.

Temperature profiles in the bed during sintering

The temperatures of the different thermocouples in the sinter bed during the test are presented in Fig. 6.

The retention time in the different zones was as follows:
- drying zone: 6 min
- reaction zone : 6 min
- cooling zone : 20 min

The drying time depends on the moisture content of the agglomerates and it should be controlled case by case. In this case the moisture content was about 15 %, which is valid for these local conditions on a commercial scale.

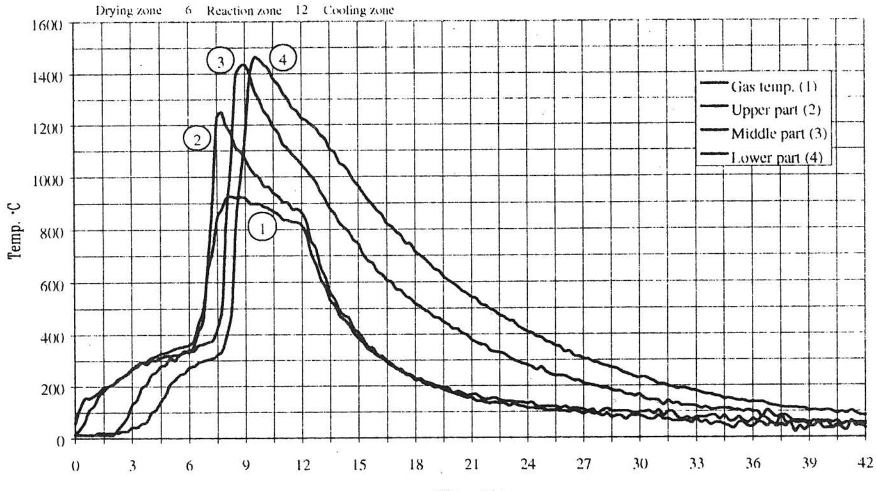

Fig. 6. The temperature profiles of the sintering test.

The temperature in the reaction zone rose very rapidly due to the strong burning of carbon. The free oxygen from the decomposition of MnO_2-compounds accelerates the burning of carbon. The maximum bed temperature was about 1450°C which was high enough to partly melt the batch. Hence the decomposition of ore volatiles and the burning gases in the porous structure of the bed and the sinter product. The bed was compressed during the test.

The retention of the bed at temperatures above 1200°C was 2-3 min, depending on the position. The surface of the bed was also at a high temperature long enough to produce good quality sinter.

The sinter product will strengthen during cooling. The cooling air was controlled based on the outlet temperature.

Sintering on a commercial scale

General

The manganese ore sintering process is a flexible process and can be constructed separately from the smelting unit due to the transportability of product sinter. Fig. 7 presents the ferromanganese smelting plant schematically. In smelting, a closed furnace and preheating are used in order to benefit from the CO-gas produced in smelting.

The steel belt is perforated, so that the process gases can penetrate through it. Process gases from the drying and reaction zones are conveyed to the process gas treatment. Dusts from gas cleaning are re-circulated to the process.

The sinter produced is crushed and transported to the storage bins. From the bins part of the sinter is conveyed back to sintering and the rest is transported to the smelting or storage area. Fines from crushing are re-circulated back to Mn-process.

If the smelting furnace is closed and equipped with CO-gas collection, the CO-gas can be used as energy in sintering, in the preheating of smelter feed and in utility areas of the smelter.

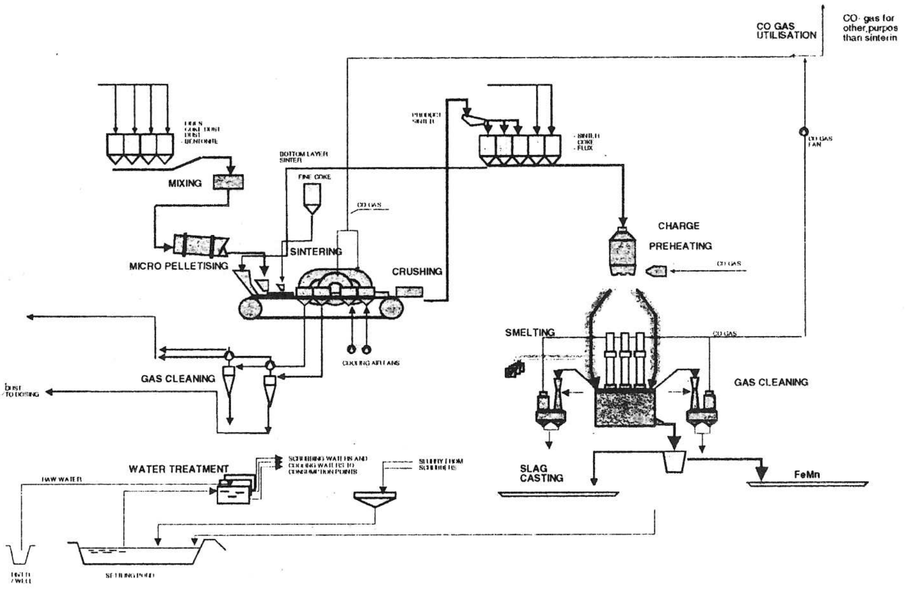

Fig. 7. Process flowsheet of the ferromanganese plant.

Before sintering, the ore fines (<10 mm) are agglomerated in a rotary drum. The bentonite is used as an agent to bind the finest particles to larger agglomerates or to the surface of the larger particles. The final moisture content of the drum product can vary relatively greatly, from about 5 to 20 %. The moisture content of the agglomerated feed can be as high as the conveyors and feeder allow.

Before the wet agglomerate is fed to the steel belt, crushed product sinter is fed to the belt in order to form a protective layer against overheating in the reaction zone.

In sintering, carbon is used as the main energy source. In steel belt sintering, the utilisation of hot, circulating cooling gases reduce the amount of carbon needed for sintering.

In primary cooling the hot porous sinter, as well as the belt protective layer, are cooled by air. In primary cooling the reoxidation reactions also release some energy to the process gas. There are no liquid phases after primary cooling. In secondary cooling mainly the cooling effect can be found.

Drying zone

In a steel belt sintering furnace, hot cooling gases are used as a secondary energy source in order to save the primary energy source, ie fine coke.

In the drying zone the secondary cooling gases (200-400 °C) are used to dry the wet feed partially. The reactions in the drying zone are mainly vaporisation of moisture and decomposition of goethite. The temperatures are relatively low, offering appropriate drying without carbon ignition and decomposition of MnO_2.

The vaporisation degree of the moisture is about 10 to 20 %, depending on the secondary cooling gas energy and process control. A high moisture content in the feed also prevents dust formation in the process gas flow.

Sintering zone

As hot gases (800-900 °C) from primary cooling pass through the partially dried feed in the sintering zone, the feed dries and the coke is ignited. During the temperature rise, the MnO_2 starts to decompose and high partial oxygen pressure is formed. Oxygen reacts with the fine coke and the temperature starts to rise very fast, finally producing a thin molten layer. Process gas and $CO_2(g)$ and $H_2O(g)$ from the reactions make the molten phase porous and the process gas can easily penetrate throughout the bed.

The hot, circulating primary cooling process gas flow drives the thin and porous molten layer downwards and solidifies the molten phase produced, resulting in porous sinter. The hot gas below the reaction layer effectively dries the feed and the reaction proceeds downwards.

Cooling zones

In primary cooling the sinter produced is cooled. The temperature of the cooling gas flow is between about 700°C and 900 °C, depending on the process gas flow and sinter temperatures. In cooling, metallic iron and some of the manganese oxides are reoxidised.

In secondary cooling the sinter is cooled in order to provide a sufficient amount of energy for drying. The temperature of the gas flow after secondary cooling is about 200-400 °C. No significant reactions occur in the secondary cooling.

Process control

The composition of the feed material gives the characteristic velocity to the reactions in sintering. The process and reactions can be controlled by the moisture content of the feed, degree of drying and amount of coke. The speed of the steel belt is dependent on the process design criteria.

The cooling is controlled by the amount of air. Due to the porous structure of the sinter produced air cooling is effective.

ADVANTAGES of the steel belt sintering process

Steel belt sintering for manganese ore fines is a continuous process with various alternatives to control the process.

The major benefits of the Outokumpu Mn-ore sintering process are, reduced energy consumption (amount of fine coke), higher submerged arc furnace availability and higher FeMn productivity, which mean high competitiveness.

Coke-saving continuous sintering process

In the manganese ore sintering process the main energy source is fine coke. The circulation of hot cooling gases lowers the amount of fine coke needed in sintering reactions. No additional fuel is required for the heating of process gases during normal operation.

Studies made suggest that about 40% less fine coke is needed than in conventional sintering.

Higher recovery of manganese

In sintering, by controlling the moisture content of the feed material, dust formation is low in drying zone and also in reaction zone due to the molten phases generated. Thus manganese recovery is increased.

The reducibility of the sinter is better compared to the direct feed of fines and lumpy ore. Due to the different reduction mechanism of the sinter, a higher reduction degree of manganese is achieved already in a solid state.

In a submerged arc furnace, with hard porous sinter charge, dust formation is much lower compared to manganese ore fines and lumpy ore charge. This is due to lower gas amounts from the furnace and a negligible amount of fine particles in the furnace charge.

The porosity of the sinter gives a large inner surface area and good reduciability. The reaction rate will also be more stable compared to the ore. The reactions take place at a regular rate, minimising great changes in furnace pressure. The reduction process is not disturbed and again manganese losses decrease.

CO-gas utilisation and charge preheating

Manganese sinter can withstand higher temperatures without losing strength. Thus the CO-gas generated in a closed smelting furnace can be utilised in the preheating of the furnace charge.

Charge preheating results in many benefits, namely considerably decreased energy consumption and stable furnace operation.

Higher availability (Submerged Electric Arc Furnace)

The reaction gases are distributed evenly through the sinter burden due to the even and porous sinter bed.

The high dust formation of manganese fines or lumpy ore clog the burden (descending of burden, crust and bridge formation) and prevent the degassing of the process, resulting in unsteady furnace operation.

A totally closed and large-size furnace can be used with a sinter charge. This results in clearly lower exhaust gas volumes compared to semiclosed or open furnaces and much smaller gas cleaning equipment. The CO-gas content in the exhaust gas will be high, which means that the gas can easily be utilised as fuel after cleaning.

In charge preheating to temperatures of 500 - 700 °C, fluxing agents for smelting are also calcined, which results in more steady furnace operation.

Furnace operation is more steady with homogeneous, free fines and dry sinter charge compared to the direct feed of fines and lumpy ore.

When smelting manganese fines and lumpy ore the molten phases occur already in the upper parts of the furnace bed. These increase the electrical conductivity of the bed and result in an unsteady state of operation. Instead of this, when smelting the sinter, the molten phase formed in the upper parts remains inside the structures, due to its porous structure and the above mentioned problems can be avoided.

Sinter and transportation

Due to its high strength sinter can withstand long-distance transportation, which offers the attractive possibility of utilising the fines in the form of sinter in other FeMn smelters either by the company or by the client.

Conclusions

Long experience of research and operation with a steel belt sintering furnace for chromite has given the new idea of also utilising this proven technology for sintering manganese ore fines.

Due to better process control and utilisation of hot cooling gases, the energy needed for sintering, in the form of fine coke is much lower than in the conventional process. The sinter produced is of even quality with strong porous structure.

Tests show that the process can be operated independently and can therefore be situated near the mine or smelter. If CO-gas is available, it can be used as fuel in sintering and decreases slightly further the amount of coke fines needed.

The steel belt sintering process can be controlled in many ways, resulting in the high recovery of manganese in sintering and in smelting.