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The ROMA project (Resource Optimization and Recovery in the Material Industry) – a typical cooperation project in Norway

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Abstract – The ROMA project is a competence project on optimizing the usage of raw materials and energy in the ferromanganese, silicon, and aluminium industries. One of the items investigated in this project is the effect of fines on the furnace, and the usage of agglomerates versus lumpy ore.

From lab-scale experiments it is shown, that for the charge to agglomerate in the furnace, the charge has to be exposed to a temperature higher than about 1200°C, independent of fines content. The fines less than 1 mm also showed higher agglomeration properties, compared to 2–4 mm, which showed no agglomeration property at all.

The properties of agglomerates are very dependent on the pre-treatment of the agglomerate. Sinter and pellets, which have been heated to high temperatures, show a better strength, but also a lower CO reactivity. Sinter also shows a lower melting temperature compared to the ore.

INTRODUCTION

The ROMA project is a typical cooperation project between academia and industry in Norway. It is a KMB project – a Knowledge-building project with user involvement. As the title indicates, the KMB project has a goal of developing knowledge and competence within the chosen area. The Norwegian industry and the Norwegian Research Council covers equal amounts of the cost. In the KMB projects, there is also an expectation from the research council that there is a high degree of publication in the project, and, hence, the research usually has a high degree of basic research.

The industry participants in the ROMA project include Al producers, Mn-alloy producers, ilmenite smelters, and Si producers. In addition, there is also Alstom, an equipment producer. The project lasts for 7 years and includes 6 PhD projects. In addition to the PhD students, the work is carried out by the Norwegian University of Science and Technology (NTNU) and SINTEF.

The major resources used in this industry are raw materials and energy. Hence, the goal of the project is to optimize or recover raw materials and energy.

When it comes to raw materials, the common feature is usage of fines. When it comes to energy, the focus is on the recovery of energy. The project is divided into four sub-projects, based on the different research disciplines and processes:

1. **Materials flow and process integration**: This part is focusing on the fines available in the Al industry. The flue gas and the particles in the flue gas are monitored and investigated. Also, recycling of waste from upgrading of secondary alumina is important and covers a PhD project. A smaller part has been to investigate whether bio-carbon materials can be used in anode production in the Al industry.
2. **Energy recovery:** This part is focusing on energy recovery for the designated industries. The challenges are the dirty gas flow and/or the low temperature of the gas.
3. **New raw materials:** The main focus of this sub-project is the utilization of fines in the manganese processes and TiO_2 smelting. In the smelting of TiO_2, equilibrium conditions at high temperature, and upgrading of fines, are essential. In ferromanganese production, the usage of agglomerates from fines is the main focus. In addition, some work is done on the effect of fines in the furnace.
4. **Junior programme:** As recruitment into the metallurgical industry is a continuous challenge, the Junior programme supports activities towards students. Examples of this are summer jobs, excursions, and other miscellaneous activities, like writing an introductory book about metallurgical processes.

In this report some of the work within <u>ferromanganese production</u> in the **New Raw Materials sub-project** will be described. The work is performed by SINTEF scientists, PhD students, and students doing their masters degree at NTNU.

USAGE OF FINES

The overall goal for the sub-project is to optimize the use of raw materials, especially regarding fines usage, and also the exploitation of new raw materials. At the same time, to get good answers, the focus must be concentrated on a few goals. The first item is the thermal conductivity of manganese sources. Various other properties of the ore have been investigated previously. However, the thermal conductivities of the most-used raw materials in manganese processes remain in need of investigation. The goal is, therefore, to measure the thermal conductivity of Mn raw materials, and to be able to tell their impact on the furnace operation. The results from this work are reported in detail in another paper at this conference.

The next items that will be discussed more thoroughly in this paper are the effect of fines in the furnace, and the properties of agglomerates versus ore.

In this project also some minor work has been done on carbon materials. First of all, some continuous work of Per Anders Eidem's PhD thesis on electrical resistivity; secondly, a summary of slag reactivity of carbon materials done by Jafar Safarian. However, this will not be discussed in this report.

Operational problems due to addition of fines in the furnace

In closed ferromanganese furnaces, the addition of fines, high-oxygen ores, and water is causing operational problems and, in a worst-case scenario, explosions[1]. Safety limits have usually been developed through many years of experience. There are, however, many questions related to this issue: Which size of the material is detrimental to the operation? Are the different types of fines (ore fines, metal fines, coke fines) equally detrimental?

In his master thesis[2], Michal Ksiazek, heated various mixtures of high-oxygen ores, ore-fines, metal-fines, and water to different temperatures to see if serious agglomeration could occur. The test parameters and his results are shown in Table I. The main conclusion was "*sinters obtained in all experiments are relatively brittle and are not dangerous for proper running of submerged arc furnace. They are not strong enough to be causing bridging or hang-up. Some of the charge composition which was used was far away from real charge mixture used in industrial conditions. In this extreme conditions we have not observed any potential dangerous from sintering formation for correct manganese production beside poor burden permeability*." Especially the 2–4 mm size fraction showed no sintering at all at 1100°C (Figure 1). When the fines where smaller than 1 mm, the sintering ability increased. Also the capability to contain water increased when the –1 mm fines were added, as seen in Table I. However, it was shown that the strong sintering only occurred when the temperature was high enough, that is above 1250°C. However, the burden permeability will decrease drastically with increasing fines content.

Figure 1: Charge with 17% 2–5mm ore fines (F-70(4-8)17-(2-4)-13(3-5)-W3,6)

Table I: Conditions for natural agglomeration

	Comilog MMA [%]			SSAB coke (3-5mm)	Temp	Metallic Fines [%]	Heating rate	Water [%]	Holding time	Sintering (0-5)
	(4.76-8mm)	(2.38-4.76mm)	(≤1mm)							
S-87(4-8)-13(3-5)	87			13%	1100ºC	0	Slow		4h	1
F-70(4-8)17-(2-4)-13(3-5)	70	17		13%	1100ºC	0	Fast		1h	0
F-70(4-8)17-(2-4)-13(3-5)-W3,6	70	17		13%	1100ºC	0	Fast	3.6	1h	0
F-70(4-8)17-(1)-13(3-5)-W8	70		17	13%	1100ºC	0	Fast	8	1h	1
F-43,5(4-8)43,5-(1)-13(3-5)-W15	43.5		43.5	13%	1100ºC	0	Fast	15	1h	2
F-43.5(4-8)43.5-(1)-13(3-5)-W16-4h	43.5		43.5	13%	1100ºC	0	Fast	16	4h	2
F-43.5(4-8)43.5-(1)-13(3-5)-W16	43.5		43.5	13%	1250ºC	0	Fast	16	1h	4
F-43.5(4-8)43.5-(1)-13(3-5)-W16	43.5		21	13%	1250ºC	21	Fast	16	1h	4
F-87(4-8)-13(3-5)	87			13%	1250ºC	0	Fast	0	1h	3
F-87(1)-13(3-5)-W16			87	13%	1250ºC	0	Fast	16	1h	4

This work is continued by investigating agglomerated samples on top of the burden in industrial furnaces. The preliminary findings are that they usually contain materials from the high temperature zone (slag spitting) and/or high amounts of alkalis. This work will be reported in Dmitry Slizovskiy's PhD thesis.

Use of agglomerates in the submerged arc furnace

The detrimental effect of fines is dependent on chemical composition, size of fines, and also on the process itself; silicomanganese versus ferromanganese, open versus closed furnace, and the size of furnace. The fines will hence usually be agglomerated to achieve a better size. Although the, by far, most used agglomeration technique for manganese ores is sintering, pelletizing and briquetting are also possible agglomeration techniques. In this paper, the properties of lump material versus sinter, pellets, and briquettes will be discussed.

When discussing the use of agglomerates in the furnace, *e.g.* lumpy ore versus sinter from the same ore, the chemical composition of the materials will mainly be the same when they reach the high-temperature zone in the furnace. After the raw materials are melted into a liquid slag, there will be small differences between the slag from an ore versus that from a sinter. The differences between these two raw materials will therefore be of interest only in the pre-reduction zone, where the raw materials are still solid, as well as in the area on top of the coke bed where the Mn-source is melting. In this paper, the following properties will be discussed:

~ CO reactivity affecting power consumption and C consumption
~ Warm strength, which is believed to affect the stability of the operation
~ Porosity, which affects the degree of pre-reduction, water content, and strength
~ Melting temperature, which might affect the temperature in the coke-bed zone, and the reduction temperature.

In this paper, the CO reactivity and warm strength are compared between lumpy ore and pellets, sinter, and briquettes from two ores[3]. The agglomerates are all made in the laboratory, and might, therefore, not be directly comparable with industrial agglomerates.

When the ore is heated to 800°C, the manganese oxides will be somewhere between MnO and Mn_3O_4. In the industrial furnace at this temperature, the reaction at the surface of the coke is sufficiently rapid to make the ore reduction reaction [1] and the 'Boudouard reaction' [2] run simultaneously. As a result, the CO_2 gas formed by reduction of Mn_3O_4 may in turn react with carbon to give the overall reaction [3]:

$$1/3\ Mn_3O_4 + 1/3\ CO = MnO + 1/3\ CO_2 \qquad \Delta H_{298} = -16.9\ kJ \qquad [1]$$

$$1/3\ C + 1/3\ CO_2 = 2/3\ CO \qquad \Delta H_{298} = +57.5\ kJ \qquad [2]$$

$$1/3\ Mn_3O_4 + 1/3\ C = MnO + 1/3\ CO \qquad \Delta H298 = +40.5\ kJ \qquad [3]$$

Table II: Oxygen left as MnO_x at 800°C for each manganese ore and agglomerate, which will lead to extra coke consumption

	Oxygen as MnO_x before experiment (analysis)	Oxygen left as MnO_x at 800°C Calculations based on CO in off-gas / weight loss	Oxygen left as MnO_x at 1100°C (analysis)	Theoretical extra consumption of coke (kg) per tonne of FeMn	Theoretical extra power consumption kWh per tonne of FeMn
Ore A	1.94	1.00 / 1.00	1.0	0	0
sinter	1.22	1.14 / 1.10	1.0	18 – 25	72 – 100
pellet	1.34	1.15 / 1.10	1.0	18 – 26	72 – 104
briquettes	1.93	1.00 / 1.01	1.0	0 – 2	0 – 8
Ore B	1.94	1.04 / 1.00	1.02	0 – 7	0 – 28
pellets	1.31	1.22 / 1.10	1.03	18 – 38	72 – 152
briquettes	1.95	1.00 / 1.01	1.0	0 – 2	0 – 8
sinter	1.27	1.11	1.03	19	76

Assuming that all of the oxygen above MnO at 800°C will react with carbon, the increase in carbon consumption and power consumption is calculated and shown in Table II. While the high-oxygen materials, the briquettes, and the lumpy ore, will be totally pre-reduced, the sinter and pellets will give about 100 kWh/t higher power consumption, due to the difference in degree of pre-reduction. There will, of course, be an uncertainty in these numbers as, first of all, the temperature of 800°C is an assumption, and, next, the heating rate and gas composition is not 100% the same as in an industrial furnace.

The thermal decomposition during heating and reduction (CI) as well as the abrasion strength (TI) is shown in Table III. At each end of the scale are the pellets, with the highest strength of the materials, and briquettes, with the lowest strength. The briquettes give around 70% -1.6 mm after the reduction and tumbling. For Ore A the sinter gives a somewhat higher strength during tumbling than the ore. This is in agreement with previous publications[4], where the sinter from Gabon has a higher tumbling strength compared to Gabonese ore.

Table III: Cohesion index and thermal stability index for the various ore and agglomerates

	Cohesion index	Thermal index
Ore A	29	61
sinter	35	80
pellet	94	96
briquettes	0	30
Ore B	14	64
pellets	96	92
briquettes	0	31

For these two ores, which are very similar in many respects, the porosity, as shown in Table IV, might explain some of the difference in CO reactivity and strength. Where the ores and briquettes show the highest porosity, they also have the highest reactivity and the lowest strength. As the porosity is lower in the sinter, the CO reactivity is higher and the strength is lower. The lowest porosity is definitely in the pellets, where the strength is highest and CO reactivity lowest.

Table IV: Absolute density and porosity for the manganese ores and agglomerates

Sample	Absolute density (g/cm3)	Porosity (%)
Ore B	4.6	18.5
briquette	3.25	22.19
sinter	3.84	11.13
pellet	4.12	4.68
Ore A	4.15	22.58
briquette	3.28	24.34
sinter	4.18	17.70
pellet	4.33	11.85

Table V: Melting characteristics of the materials compared to melting temperature of ore (no replicas)

Material	Start melting	Start reduction	Finish melting
Ore B	Ref.	21	146
briquette	-44	-36	146
sinter	-81	29	263
pellet	-4	13	221
Ore A	Ref.	47	165
briquette	-203	-184	50
sinter	-94	-85	97
pellet	-159	-133	65

The melting temperature of the ore may be an important factor affecting the temperature in the high-temperature area of the furnace. The melting temperature is affected by the chemical composition, the mineralogy, and the grain size of the minerals. When considering the concept of a melting temperature, both the liquidus composition as well as the reduction rate is of importance. A few introductory melting experiments were performed in a sessile drop furnace (Table V). Although there are no conclusive data, due to no replicas, all the agglomerates melt at a lower temperature compared to the ore. Both sinters melt at about 100 K lower temperature. This is in accordance with previous publications; Gaal *et al.* [5] found that comparing CVRD sinter and CVRD ore, the sinter starts to melt and reduce at lower temperatures. The reduction of the sinter starts about 100°C lower temperature compared to the ore. Also, experiments with industrial-sized particles show that the sinter is melted and reduced at a lower temperature[6]. In accordance with sessile drop experiments, also here the difference in melting and reduction is about 100°C between ore and sinter.

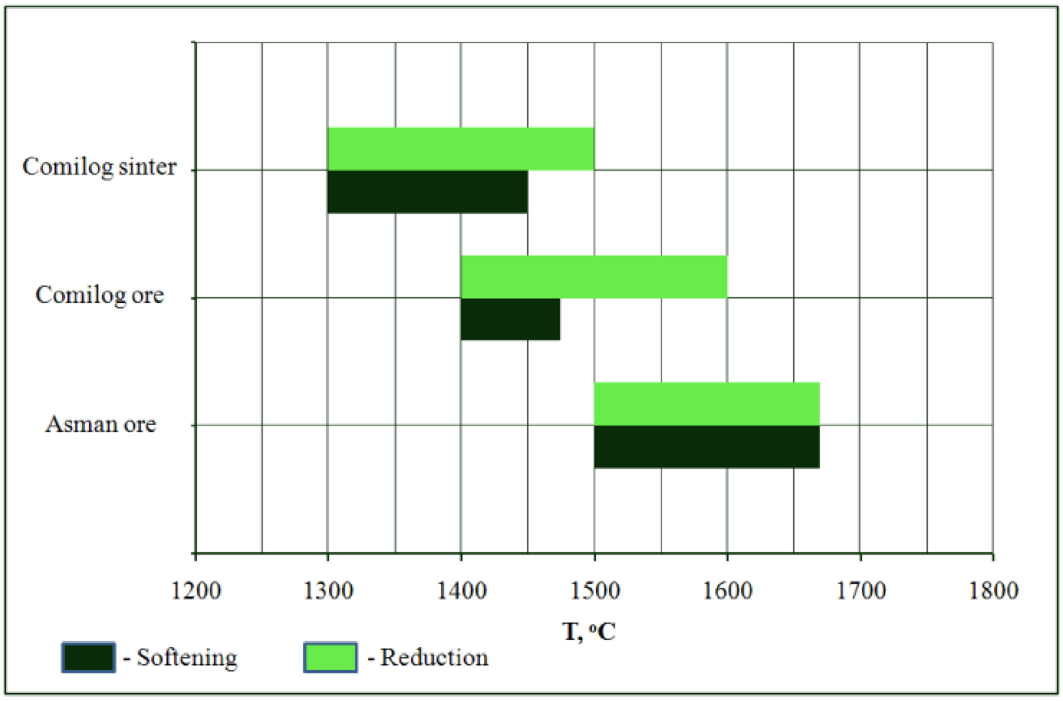

Figure 2: Comparison of melting and reduction temperature for Comilog ore, Comilog sinter, and Asman ore[6]

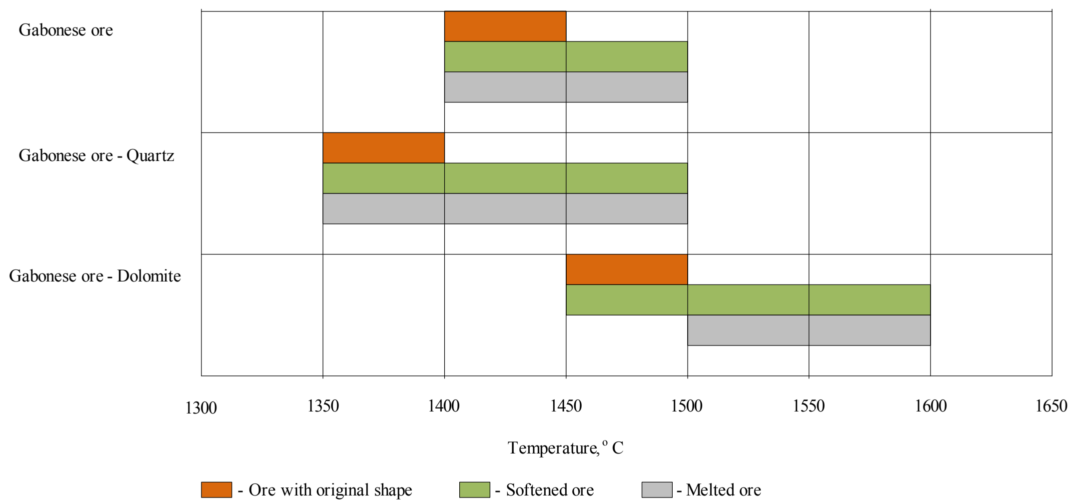

Figure 3: Comparison of melting and reduction temperature for Comilog ore mixed with quartz or dolomite[7]

The temperature where the reduction starts, and flow into the coke bed, is not only dependent on Mn-source. The flux added will mix with the ore, and affect both the flow properties as well as the reduction rate. The so-called 'melting temperature' may affect the temperature in the coke-bed zone, as can be seen in Figure 3. When mixing a Mn ore with dolomite, more solid MnO phase will be present, and hence the reducibility will decrease and viscosity increase. However, whether a high-melting temperature is beneficial or detrimental to the operation may be discussed. Although one may believe that a high melting temperature will give a high temperature in the coke bed, and hence good reducing conditions, several SiMn furnaces operate with high quantities of low-melting HC FeMn slag. Therefore, these matters need to be clarified further.

CONCLUSIONS

The ROMA project is a competence project on optimizing the usage of raw materials and energy in the ferromanganese, silicon, and aluminium industries. One of the items investigated in this project is the effect of fines on the furnace, and the usage of lumpy ore versus agglomerates.

From lab-scale experiments, it is shown, for the charge to agglomerate in the furnace, the charge has to be exposed to a temperature higher than about 1200°C, no matter how much fines was added. The fines less than 1 mm also showed higher agglomeration properties, compared to 2–4 mm, which showed no agglomeration property at all.

The properties of agglomerates are very dependent on the pre-treatment of the agglomerate. Sinter and pellets, which have been heated to high temperatures, show a better strength, but also a lower CO reactivity. Sinter also shows a lower melting temperature compared to the ore.

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REFERENCES

1. G. Pochar, L. Joncourt, N. Touchard, and C. Perdon, Metallurgical Benefit of Reactive High Grade Ore in Manganese Alloys Manufacturing, *INFACON XI*, New Delhi, India, 18–21 February 2007, pp.217–230.
2. M. Ksiazek, Causes and Mechanism of sintering phenomenon, Master Thesis, AGH, 2008.
3. M.Tangstad, D. Leroy, and E. Ringdalen, Behavior of agglomerates in ferromanganese production, *Infacon XII*, Helsinki, 2010.
4. M. Tangstad, P. Calvert, H. Brun, and A.G. Lindseth, Use of Comilog Ore in Ferromanganese Production, *INFACON 10*, Cape Town, South Africa, 2004, pp.213–222.
5. S. Gaal, E. Ringdalen, D. Vaganov, and M. Tangstad, Melting phenomenon of manganese bearing ores, *VIII Int. Conf. Molten Slags, Fluxes and Salts*, Chile, 18–21 January 2009.
6. D. Slizovskiy, M. Tangstad, and S. Wasbø, Melting temperatures of ore for manganese process, To be published in 2011 in Canadian Metallurgical Quarterly.
7. B. Xakalashe, Conditions for smelting of manganese ore for ferromanganese production, *NTNU-student report*, October 2010.

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