THE SMELTING OF MANGANESE CARBONATE ORE

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ABSTRACT

The practice of manganese ferroalloy smelting has traditionally been based on utilising oxide ores which typically contain a high level of manganese. This preference for oxides has even been extended to the modification of natural carbonates into nodulized oxides. However smelting practices developed over the past 30 years have created a market for natural manganese carbonate ores, driven in part by the unique properties that this type of ore can offer.

An understanding of the mineralogy of carbonate ore and its thermal properties has provided important information which enables furnace operators to take full advantage of the chemical differences. However changes to traditional operating practices have been necessary. Once furnace operations using natural and unmodified carbonate ore have been mastered, the unique chemical features of manganese carbonate ore are able to contribute, not only to new product development, but also to cost savings.

The use of natural manganese carbonate ore is now a well-established aspect of the industry. The sustained increase in demand for carbonate ore worldwide over the past several years confirms acceptance of its quality. There are effectively few limits to its successful use.

1. INTRODUCTION

Manganese oxide ores have traditionally been the principal source of supply for alloy smelting. At the beginning of the 20th century, the main suppliers were Georgia, India and Brazil. As the steel industry expanded, so also did manganese ore mining activity and the acceptance of ores containing less than 50% Mn. The steelmaking centres of the world by 1910 were Western Europe (principally Germany, Britain, France and Belgium), the Austro-Hungarian Empire, Russia and the USA. Total production in that year was about 60 million tons. Steelmaking in the Far East was at a very low level. In the Western Sphere, it was only the USA which had the potential to exploit domestic manganese ore resources. Manganese ore has always been a seaborne supply industry.

The first commercial source of manganese carbonate ore was that recovered from the tailings of lead-zinc ore processing in Montana, USA; the manganese was not the primary resource. In this operation, the flotation tailings contained micron-sized rhodochrosite which analysed about 38% Mn and 6% SiO_2, but was fine sized which meant that it was not directly useable. Anaconda developed a size-enlargement process called nodulising, in which the slurried tailings were calcined in the first stage of a rotary kiln. Raising the temperature further at the discharge end of the kiln up to that for material softening allowed the natural tumbling action to induce accretion build-ups. The product was a hard and lumpy material analysing over 50% Mn. The primary purpose of this nodulising operation was for size-enlargement. While calcination was an integral part of the process, it is possible that the removal of zinc by volatilisation was necessary at that time to meet the standard specification for manganese ore. [1,2,3,4] This operation, which was primarily a war-time development, eventually ceased in 1964 as the availability of natural lumpy ores increased in the second half of the 20th century.

The economic viability of the nodulising process requires low-cost energy, which was available in the USA at that time as natural gas. A similar nodulising operation was started in Mexico in the 1960s, again based upon low-cost natural gas. The difference to the Anaconda operation was, however, that this time the manganese carbonate ore was the principal mined product, not derived as a by-product.

The purpose of the Mexican development was also different in that it was necessary to upgrade by calcination the run-of-mine ore, which analysed only 27% Mn, into a product containing almost 40% Mn [5] in order to lower the cost of transportation to a coastal smelter. In both of these nodulising operations, it was never the intention to use the raw carbonate ore directly in ferroalloy smelting, and the justifications for processing were primarily size-enlargement in Montana and reduced transportation costs in Mexico. A third nodulising plant using the same technology was built in the late 1970s at the Nusta mine in Ghana. This operation was designed to burn fuel oil. This fuel type, together with the lack of any realistic energy options, has prevented the establishment of nodulising operations in Ghana.

There has always been a role for carbonate ore in the manganese industry. However since pure $MnCO_3$ contains 47.7% Mn, it is evident that commercially available natural carbonate ores will only contain about 30% Mn because of the presence of quartz and dolomite associated with the manganese mineral. It is this feature of carbonates which has often given rise to the “low grade” designation assigned to them. However carbonates, in which the principal manganese mineral is rhodochrosite, do indeed have unique features which distinguish them completely from oxide ores. Table 1 below provides some details of several carbonate ores that are or have been commercially available:

Table 1. Examples of Manganese Carbonate Ores.

	%Mn	%Fe	%P	%SiO_2	%Al_2O_3	%CaO	%MgO	%H_2O
USA [4]	24-26	1.5-2.5	0.40	25-33	2-3	2-5	1-3	n.a.
Nsuta	29-33	0.7-0.9	0.05-0.07	10-14	1.5-3.0	4-6	3-6	1-2
Molango [5]	27.7	5.9	0.06	9.0	n.a.	5.6	7.0	n.a.
Amapa	31-35	3.5-5.5	0.04-0.05	10-20	1.5-3.5	3-4	2-4	n.a.
China	20-30	3-5	0.15-0.25	14-22	n.a.	n.a.	n.a.	n.a.
Bulgaria	30-33	1-2	0.13-0.15	10-14	n.a.	4-7	2-4	10-20
Ukraine	27-31	2-3	0.20-0.25	20-25	2-3	4-5	1-2	n.a.
Georgia [6]	11-32	n.a.	0.05-0.50	7-39	n.a.	4-26	n.a.	n.a.

Note: n.a. denotes data is not available.

Carbonate ore mining was carried out in Japan for many years, but ceased in the early 1970s, to be replaced by ore imported from Ghana. The Amapa deposit has been abandoned as uneconomic for further development. The supply of Molango nodules to the Autlan smelter in Tampico, Mexico, has on occasion been interrupted during periods of high energy costs, such as the North American energy crisis in 2001. Chinese carbonates are generally melted in a cupola or small blast furnace, and then tapped as a high grade slag which is crushed and screened before charging to the ferroalloy furnaces – an expensive raw material even in China. The Bulgarian ore is soft and not useable in ferroalloy production without prior processing. The carbonates from Ukraine and Georgia are generally not utilised separately because they do not provide significant advantages over the local oxide ores.

It is noted here that the manganese bearing mineral in the South African Mamatwan and Gloria deposits, mined respectively by BHP-Billiton and Assmang, exists principally as the silicate. The carbonate component of this deposit is limited to the presence of limestone and dolomite. Geological reports do not record these ores as manganese carbonates [7,8], and therefore their performance during smelting will be quite different to that of rhodochrosite ore.

The first record of using unprocessed carbonate ore directly in electric furnace ferroalloy production was of material from the Nsuta mine in Ghana. Prior to nationalisation in 1971, the mine had been owned by the Union Carbide Corporation and this company successfully tested the ore in their own ferroalloy plants. Union Carbide confirmed after trials during the 1960s in the USA that Nsuta carbonate ore was suitable for direct smelting [9], and the mine then supplied carbonate ore to Union Carbide’s and later Elkem’s smelters in Norway during the 1970s and early 1980s. Since privatization of the Nsuta mine in 1995, carbonate ore has been successfully introduced by the Ghana Manganese Company (GMC) to other ferroalloy producers in Western and Eastern Europe, the CIS and the Far East. In the mid 1990s, a new plant in the Middle East commenced operations using a high percentage of Nsuta carbonate ore in the raw material blend, and the metallurgical performance confirmed the results achieved by the Union Carbide Corporation almost 30 years before.

2. PHYSICAL AND CHEMICAL PROPERTIES

Since ferroalloy smelting requires raw materials with a satisfactory combination of physical and chemical properties, it is readily apparent from the analyses recorded in Table 1, that GMC Nsuta carbonate is the only ore of this type which has a combination of the following qualities:

- high Mn:Fe ratio
- high Mn:P ratio
- low moisture content

These qualities enable operators to utilise Nsuta carbonate as a blending ore, complementing oxide ores which often have higher levels of iron (Fe) or phosphorus (P), or have higher moisture contents. Recent developments in seaborne manganese ore supply demonstrate that the ferroalloy producers have come to appreciate the unique qualities of Nsuta carbonate. This paper therefore concentrates on the properties and applications of the Nsuta carbonate ore because it is the only ore of its type which is commercially available at this time to the ferroalloy industry worldwide.

2.1 Mineralogy

The major mineral species of the Nsuta carbonate listed in Table 2 have been identified by XRD analysis.

Table 2. Mineralogy of Nusta Carbonate Ore.

Mineral	Principal chemical analysis
Rhodochrosite	$MnCO_3$
Quartz	$SiO_2.Al_2O_3$
Dolomite	$MgCO_3.CaCO_3$
Calcite	$CaCO_3$

SEM analysis confirms that the ore consists of a fine-grained carbonate phase embedded with quartz of a similar or slightly larger size.

2.2 Strength

The Bond Work Index was determined using the standard laboratory procedure to be 12.4, in units of kWh per short ton. Table 3 provides a comparison of Nsuta rhodochrosite with other common minerals.

Table 3. Bond Work Index Values.

Limestone	9.9
Hematite	11.1
Nsuta carbonate	12.4
Magnetite	13.2
Dolomite	13.9
Quartz	14.4

The Bond Work Index value, together with the Standard ISO Tumble Test result of less than 7%, confirms the hardness and resistance to abrasion of Nsuta carbonate. Repeated handling generates only a minimum of fines.

2.3 Bulk Density

The bulk density of the Nusta carbonate, as is the case for other materials, varies depending on its sizing. Standard lump 100 x 10 mm material has a bulk density of 1.7 to 1.8 tons /m^3. Typical crusher fines have a bulk density of 1.9 to 2.0 tons /m^3.

2.4 Thermal Characteristics

Combined thermo-gravimetric (TG) and differential thermal (DT) analysis in an inert gas atmosphere over the temperature range of 20°C to 1,200°C, as shown in Figure 1, has identified that:

- A weight loss of 35% is attained in two distinct stages. Weight loss of 31% is achieved in the temperature range of 415°C to 730°C. A further 4% of weight loss occurs between 730°C and 1,200°C.
- The endothermal peaks at 622°C, 645°C and 791°C indicate that three different reactions take place during decomposition. These reactions are expected to be related to the dissociation and calcination of various combinations of carbonates, according to the following reactions:

$$\mathrm{MgCO_3 = MgO + CO_2} \tag{1}$$

$$\mathrm{MnCO_3 = MnO + CO_2} \tag{2}$$

$$\mathrm{FeCO_3 = FeO + CO_2} \tag{3}$$

$$\mathrm{CaCO_3 = CaO + CO_2} \tag{4}$$

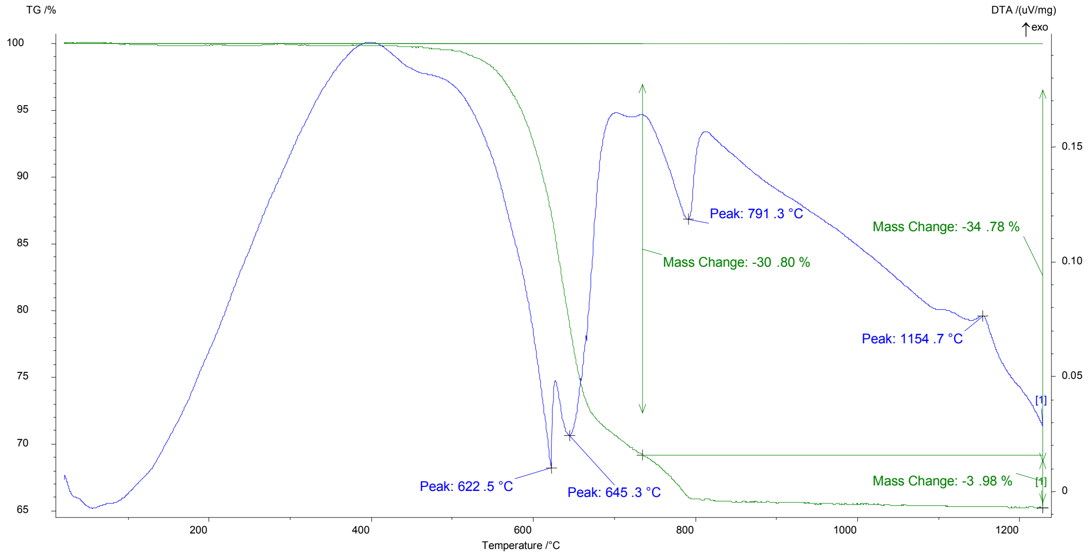

Figure 1. DTA – TGA Analysis of Nusta Carbonate Ore.

The temperature for calcination of natural limestone is significantly higher than that at which $CaCO_3$ contained in Nsuta carbonate actually decomposes because the carbonate phase is a solid solution of $(Mn,Ca,Mg)CO_3$.

2.5 Loss on Ignition

The loss on ignition value for Nsuta carbonate ore is commonly given as 29% at 900°C. This standard test is carried out in a muffle furnace without an inert gas atmosphere. Since MnO oxidises in the presence of air at a temperature greater than 600°C, it is to be expected that an LOI value less than that of weight loss as determined by TG/DT analysis is due to the partial reoxidation of MnO and FeO to Mn_3O_4 and Fe_3O_4. Therefore the standard LOI value for Nusta carbonate understates the CO_2 content of the ore.

2.6 Chemical analysis

The most representative chemical analysis for the Nusta carbonate ore has been collected from a large number of samples and is given in Table 4.

The general characteristics of the Nusta carbonate ore are that:

- % CaO is the same as or greater than the % MgO
- $SiO_2 : Al_2O_3$ ratio is approximately constant
- Mn^{2+} (or $MnCO_3$) varies inversely with the SiO_2

Table 4. Nsuta Carbonate Ore.

	Chemical analysis	Mineralogical analysis
Mn^{2+}	30.5%	
Mn^{4+}	Nil	
$MnCO_3$		63.8%
MnO_2		Nil
Fe	0.7%	
$FeCO_3$		1.5%
MgO	4.8%	
$MgCO_3$		10.1%
CaO	5.5%	
$CaCO_3$		9.8%
SiO_2	12.0%	12.0%
Al_2O_3	2.2%	2.2%
Sub-total		99.4%

3. PRINCIPLES FOR SMELTING CARBONATE ORE

Since the decomposition of natural carbonate ore in a smelting furnace occurs in a reducing environment, this calcination process allows the manganese to remain in its lowest oxidation state until it is reacted with carbon [5].

The sequence of reactions is as follows:

$$MnCO_3 = MnO + CO_{2\,(gas)} \tag{5}$$

$$MnO + C = Mn + CO_{(gas)} \tag{6}$$

This sequence of reactions is superimposed onto a furnace schematic as shown in Figure 2.

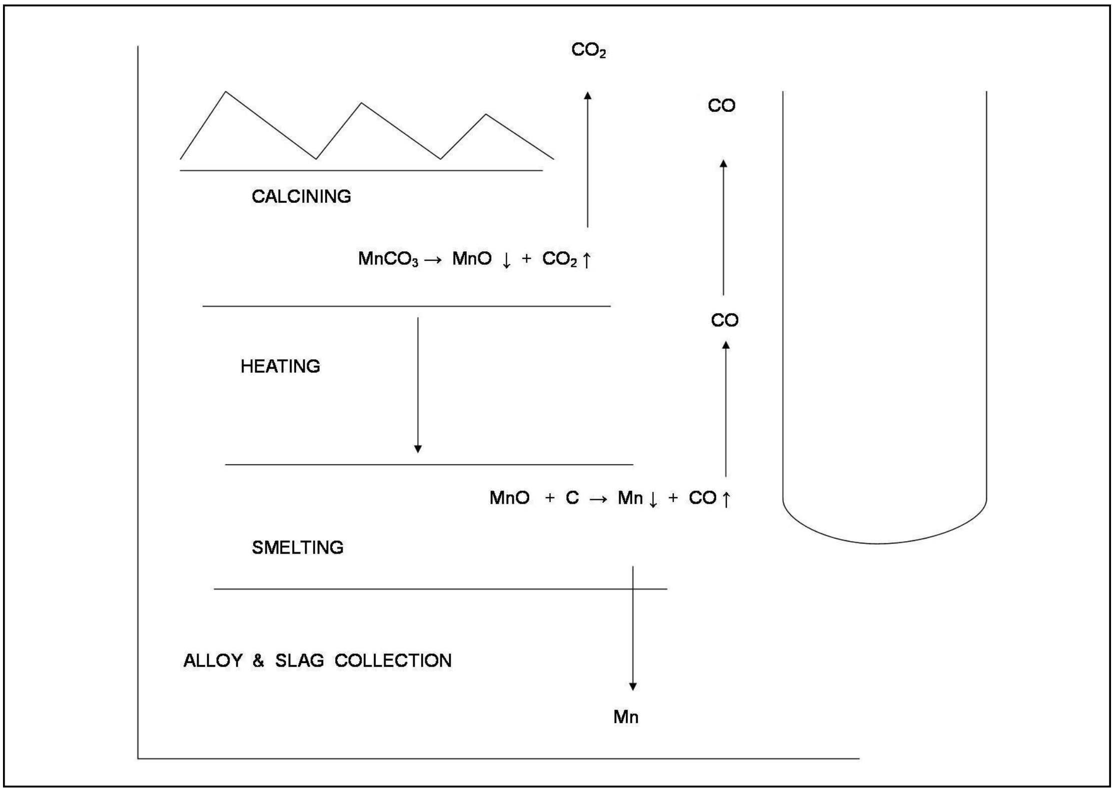

Figure 2. Furnace Schematic.

The Boudouard reaction:

$$CO_{2\,(gas)} + C = 2CO \qquad (7)$$

is strongly endothermic and only proceeds at any meaningful rate at a temperature in excess of 1,000^{o}C.[10,11] Since the Nsuta carbonate decomposes in a reducing environment at a temperature below 700^{o}C, it would appear that there is no possibility for the CO_2 gas which is released during calcination to react with carbon in the coke, but will be discharged directly to the stack. As a result, the reduction reactions for carbonate and oxide ores may be compared as follows, assuming that higher oxides have been prereduced by carbon monoxide (CO) gas:

from oxides: $Mn_3O_4 + 4C = 3Mn + 4CO$ (8)

from carbonates: $3MnO + 3C = 3Mn + 3CO$ (9)

It can be seen that carbonate ore needs 25 percent less carbon per unit of manganese when compared with the standard mixed oxide, Mn_3O_4. The lowering of the fixed carbon per unit of manganese processed increases furnace charge resistivity and therefore enhances furnace productivity. This unique feature of carbonate ore must be considered when making the transition from regular oxide smelting to carbonate ore processing.

Optimum placement of the electrode tips (the point of highest temperature and chemical activity) on or in the coke bed, (and not in or through the coke bed), will of course permit operators to optimise the quantity of reductant carbon consumed from coke and coal compared to electrode carbon that might inadvertently be used as a reductant.

4. PRACTICAL APPLICATIONS OF CARBONATE ORE

There is no manganese ore mined in Korea. As a result, the Korean manganese ferroalloy industry is based solely on imported ores. Demand for ferroalloys in Korea is greater than domestic production capacity. Hence the local ferroalloy producers must compete with imported alloys in terms of quality and price, as well as relying upon manganese miners worldwide for all of their principal raw material. The main manganese alloy suppliers to Korea in 2002 were China and Russia. The major manganese ore suppliers to Korea were Australia, Brazil, Gabon and India; all oxide miners.

The Dongil Ferroalloy Company started operations at a site in Pohang in 1975. The company now operates 6 furnaces with ratings of between 5 MVA and 15 MVA producing manganese ferroalloys to specifications listed in Table 5. The plant is in full compliance with Korean environmental standards and is routinely monitored. The raw material stockyard is enclosed by a 5 metre high fence to prevent the dispersal of wind-blown dust from the stockpiles. All delivery trucks pass through a wheel wash unit. The plant maintains a high level of cleanliness.

Table 5. Dongil Ferroalloy Company product specifications.

	%Mn	%Si	%C	%P	%S
HCFeMn	75.0	0.15-0.50	6.5-7.0	0.20	0.01
SiMn 1	70.0	16.0	1.8	0.20	0.01
SiMn 4	60.0	14.0	2.0	0.20	0.01
LCSiMn	57.0	26.0	0.5	0.10	0.01
ULCSiMn	58.0	28.0	0.1	0.10	0.01

Since Dongil purchases manganese oxide ores from all of the major suppliers in the world, the company has developed considerable expertise in ore blending practices. It was with this operational experience that Nsuta carbonate ore was first tested in 2001. At the outset, low levels of carbonate were used in the production of HCFeMn, SiMn1 and SiMn4 alloys, and this stage was successfully completed. However the development of the SiMn1 market required new raw material options because its production traditionally relied upon in-plant and purchased HCFeMn slags to blend with standard oxide ores. As working practices were optimised, it was found that the same ore blends incorporating carbonate could be used to good effect for SiMn4 production as well, since both alloys have similar Mn:Si ratios. The only difference in production practice was to vary the quantity of millscale, an in-house material from Dongil's steel rolling operations.

One change to operating practice was to raise the secondary voltage (lower the secondary current) since operating at the same current with carbonate as with oxide in the ore blend counters the advantage of higher charge resisitivity. Therefore one of the operating adjustments implemented by Dongil to make best use of the Nsuta carbonate was to lower the current setpoints. The positive effects of this move may be seen in some campaign results listed in Table 6 and Table 7.

Table 6. SiMn4 Production Data.

Period	Oxide in blend	Carbonate in blend	Slag in blend	Current setpoint (1-100 scale)	Excess Fixed Carbon	kWh/t	Mn yield	Slag: alloy ratio
Sep/02	30%	50%	20%	100	1.17	3,600	72%	1.25:1
Nov/02	20%	60%	20%	92	1.09	3,800	78%	1.14:1
Dec/02	20%	40%	40%	92	1.01	3,500	87%	0.98:1
Jan/03	60%	Nil	40%	92	1.02	3,400	75%	1.10:1

This data indicates that operating with a minimum of excess fixed carbon, which in itself requires a fundamental understanding of the behaviour of the oxide and carbonate ores, leads also to a lowering of the unit power consumption. In addition, a high manganese yield generally correlates with a minimum of excess fixed carbon and increased operating resistance, after taking into account the well documented influences of slag basisity and slag to alloy ratio. It is this balance between the level of excess fixed carbon and secondary current, and as a result the Westly C3 factor [12], which becomes critical in maintaining a high Mn yield and a low unit power consumption.

Table 7. SiMn1 Production Data.

Period	Oxide in blend	Carbonate in blend	Slag in blend	Current setpoint (1-100 scale)	Excess Fixed Carbon	kWh/t	Mn yield	Slag: alloy ratio
Sep/02	20%	60%	20%	94	1.13	4,000	84%	1.05:1
Oct/02	20%	60%	20%	97	1.13	4,000	90%	1.02:1
Jan/03	60%	Nil	40%	92	1.03	3,600	82%	1.00:1

While more work is still required to optimise the unit power consumption, it will be evident that a high manganese yield when using carbonate ore provides for a significant cost savings in ore, coke and power, as well as enhancing furnace productivity. The efficient application of carbonate ore provides excellent furnace operating conditions, despite the low manganese content of the ore.

5. CONCLUSIONS

This overview of carbonate ore smelting demonstrates that:

- There is a history of carbonate ore consumption in the ferroalloy industry, albeit limited by the number of supply sources
- The properties of Nsuta carbonate ore are consistent with the needs of this industry and provide some unique qualities which introduce an extra degree of raw material flexibility to the operators
- Precise adjustment of smelting furnace parameters results in excellent performance using a high level of carbonate ore in any blend with oxide ores and slags.

The authors wish to thank the Dongil Ferroalloy Company for permission to publish results. The authors also acknowledge the cooperation of the Ghana Manganese Company in the preparation of this paper. Since the emergence of the privatised mining company in late 1995, sales of carbonate ore to electric smelting companies producing manganese ferroalloys have increased by more than 20 times through stimulating practical discussions with end-users on how to apply these principles.

6. REFERENCES

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