Process update

Direct reduction process using fines and with reduced CO$_2$ emission

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A direct reduction process for refractory oxides and a life cycle analysis comparison with conventional pelletising and sintering process for chargechrome are presented. The new route has potential to reduce the environmental impact of the ferroalloy industry and to extend the use of non-renewable resources by utilising waste that is not economically recoverable by conventional technologies; increasing metal recoveries; significantly reducing CO$_2$ emissions; reducing or eliminating the use of coke; and reducing electricity consumption during smelting.

In South African mining operations for iron, manganese and chromite ores, considerable amounts of fine material are generated. Fine material can also be produced during the beneficiation of low grade deposits. Processes designed to treat this increasing quantity of fines are consequently becoming more important. In addition, with considerable quantities of discard materials becoming available, there is a need for a process that can recover locked-in metal values.

At the same time, the possibility of a direct reduction process for refractory ores is of interest to South African ferroalloy users because of the advantages of lower electrical energy demand and lower carbon consumption in the smelter. These will translate into lower cost ferroalloys for the steelmaker. Added to that is the potential to increase metal recoveries and furnace throughput.

The Council for Scientific and Industrial Research (CSIR) is developing a direct reduction process for fine materials that has been tested on LG6 seam chromite ores and manganese ores, but is not restricted

to these. The total energy requirement for heating and for the endothermic reduction reactions is supplied by the addition of fine coal. Laboratory tests have proved that metallisation levels in chromite reduction can be above 90% routinely for Cr (Table 1) and in manganese ore treatment there is almost complete reduction of Mn (Fig. 2). This application would be suitable not only for fine ores, but also for any in-plant wastes.

In addition to the LG6 seam chromites, there are vast quantities of chromium bearing UG2 seam discard materials from platinum mining that could be treated.

Background

Processes for direct reduced **iron** (DRI) are well known and there are many variants available.[1] These processes offer the steelmaker,[2] among other advantages, a low residuals content and the possibility of replacing scrap at times of shortage. By far the greatest tonnage of DRI is made via the Midrex route, relying on natural gas. In South Africa, with little natural gas available, coal based reduction in rotary kilns is practised and relies on lump coal. In the Corex process, in which gas based reduction is carried out, lump coal is the original energy supply. Few processes utilise fine coal, of which there is an abundant supply in South Africa. The rotary hearth process is one and two such units are currently in operation in Japan: one at Nippon Steel and another at Kobe Steel.[3]

Direct reduction for **ferroalloy** production offers substantial advantages, not least the reduction of the process electrical requirement during final smelting. Because of the difficulty of reducing refractory oxides, few processes are in operation. Two processes used in South Africa offer partial pre-reduction before smelting. The Samancor Ferrochrome Plant at Middelburg[4] is one of few plants worldwide able to produce both chargechrome and low carbon

ferrochrome; the bulk of production is supplied to the adjacent Columbus Stainless Steel plant. Production is carried out with a mixed ore and coal charge in a rotary kiln (CDR) and the product passed to a dc arc furnace for final smelting. The intent is to use metallurgical grade ore concentrates and achieve high recoveries. It is known that accretion formation at the elevated temperatures used causes operational problems.

In the Showa Denka process at Lydenburg[5] ore and carbonaceous material are milled and pelletised and are then fed into a rotary kiln. Temperatures >1290°C are used and good control of temperature is required because softening of the charge materials can cause accretion formation. Combined reduction levels of about 60% are achieved. The partially reduced pellets are sent for hot charging to a smelter unit. Both these processes achieve substantial lowering of the process electrical requirements during smelting, although the levels of metallurgical reduction for chromium and iron combined are 60–70%.

Because of the problems with softening and accretion in the kiln at elevated temperatures, lower temperatures are used, with a lowering of conversion levels.

There is no direct reduction process for **manganese**, although partial prereduction of fine ores is carried out in the manufacture of Mn metal by electrolysis.[6] The refractoriness of Mn oxide means that the temperatures required for reasonable rates of reduction in a direct process would be above the melting point of the Mn carbide alloy.

CSIR was also actively developing a two step selective process[7] to recover **titanium** from slag dumps.

CSIR concept

To overcome the problems of softening and accretion formation, to achieve a higher level of reduction and to make use of the fine materials generated

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during mining or during processing, CSIR has derived a direct reduction concept that consists of an indirectly heated tunnel kiln, in which agglomerated fine material can be processed at temperatures up to 1400°C without problems caused by softening or sticking. No other type of kiln has been identified in the literature that can process such materials continuously in the solid state at elevated temperatures without the formation of accretions that eventually lead to shut-downs for cleaning and maintenance.

A number of other advantages derived from the inherent design of the tunnel kiln render it suitable for applications where the avoidance of accretion formation is not critical, e.g. DRI production or other mineral extraction processes.

The design (Fig. 1) is similar to the tunnel kilns used in the ceramic and brick industries, but with the following main differences:

- the atmosphere in the kiln is highly reducing
- the kiln is heated indirectly by combusting the offgas from the reduction process in a chamber separated from the reduction chamber by a heat resistant ceramic partition formed from silicon carbide tiles that can withstand temperatures up to 1700°C. Consequently, little process electricity is required
- the feed to the kiln is indirectly preheated by recovering sensible heat from the combustion gases via an in-built heat exchanger
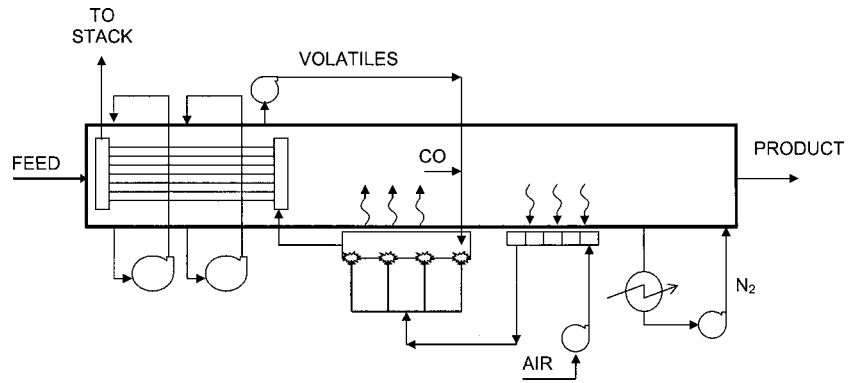
1 Schematic representation of CSIR tunnel kiln

- before the feed material enters the kiln, it is agglomerated into shapes designed both to facilitate heat transfer (convective and radiative) to the material; and to confer dimensional stability during processing.

Suitable feed mixtures (i.e. the minerals to be reduced, coal reductants, binders and fluxes) are agglomerated and dried before being stacked onto kiln cars and fed into the kiln in a semi-continuous manner via a double-door chamber that provides a seal. The kiln is operated as a pusher-type furnace.

As the material moves through the kiln, it is heated convectively by energy recovered via a heat exchanger from the hot combustion gases leaving the system. The rate of heat transfer is improved by circulating the process gases with fans, through the heat exchanger and over the material stacked on the kiln cars.

As the temperature of the material rises, volatile components are released from the coal reductant. These volatiles flow co-currently with the material into the kiln. In this way, condensation of oils and tars is prevented and the volatile components are cracked as the temperature increases. The material is preheated by convection to 600–800°C. The volatiles released from the coal are withdrawn from the kiln and fed to a combustion chamber where they are mixed with carbon monoxide produced during the reduction process and combusted with air.

The material is further heated by radiation until hot enough to react with the reductant, producing reduced material and carbon monoxide. Energy for this endothermic reaction is supplied by burning the offgases in the combustion chamber. To ensure that sufficient energy is available for the reduction reactions, the combustion air can be preheated by recovering heat indirectly from the hot product.

The reduced material must be cooled before exposure to air, preferably under nitrogen to avoid reoxidation. Nitrogen is therefore circulated counter to the

Table 1 Chemical analyses of chromite ores before and after reduction tests, wt-%: all trials at 1400°C

| Sample | Cr_{tot} | Cr_2O_3 | Cr_{met} | Fe_{tot} | FeO | Fe_{met} | Metallisation, % | | |
							Cr	Fe	Total
1	29·2	0·7	28·7	22·4	0·2	22·2	98·4%	99·2%	98·8%
2	35·1	1·8	33·9	25·4	1·0	24·6	96·6%	96·9%	96·7%
3	35·8	2·5	34·1	25·4	1·2	24·5	95·3%	96·5%	95·8%

	SiO_2	CaO	MgO	Al_2O_3	TiO_2	V_2O_3	NiO	MnO	CoO
1	9·1	0·40	9·1	17·8	0·63	0·33	0·13	0·25	0·034
2	6·4	0·20	9·2	17·0	0·63	0·42	0·16	0·24	0·046
3	6·3	0·40	9·2	16·7	0·63	0·40	0·18	0·25	0·041

	Ti	V	Ni	Mn	Co	C	S		
1	0·49	0·20	0·090	0·20	0·027	…	…		
2	0·49	0·25	0·110	0·19	0·036	4·7	0·074		
3	0·49	0·24	0·120	0·20	0·032	4·9	0·070		

1	Carbon ratio 2·00, 5% binder, ore and coal milled
2	Carbon ratio 1·33, 3% binder, ore and coal unmilled
3	Carbon ratio 1·33, 3% binder, ore and coal unmilled

Analysis by kind permission of BHP Billiton.

direction of material flow through the kiln and cooled externally. A small feed of nitrogen is introduced as make-up. Once the material has cooled sufficiently, it leaves the kiln via a double door chamber similar to that on the inlet side.
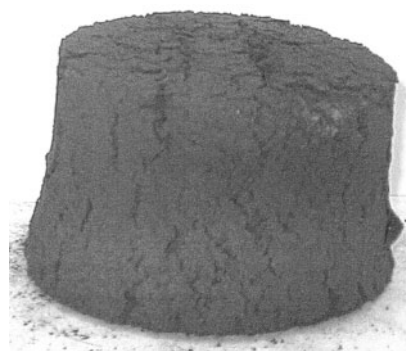
The kiln is expected to be about 120 m in length.

Proof of concept

Reduction tests have been carried out on chromite and manganese ores. Metallisation levels for Cr were >90% routinely and when very fine material was used 98% was achieved (Table 1). The tests were carried out in a high temperature furnace at 1400°C under a carbon monoxide atmosphere.

For manganese ores, high levels of metallisation were obtained. However, these were not quantified because of a difficulty in chemical analysis, i.e. inability to determine manganese and iron of different valence states in mixed samples, and consequently the results are based on mass loss data. The effect of holding time at temperatures of 1375°C was quantified in tests conducted under carbon monoxide. For times >6 h, at least 95% reduction could be obtained. The effect of treatment temperature was quantified for a holding time of 6 h in similar experiments (Fig. 2). The sudden change in reduction between 1325 and 1350°C could be due to either of two phenomenon.

Liquid phases in the MnO–SiO_2 system include the orthosilicate (Mn_2SiO_4) with a congruent melting point of 1345°C, the metasilicate ($MnSiO_3$) eutectic with Mn_2SiO_4 at 1251°C and the Mn_2SiO_4–MnO eutectic at 1315°C. Under the present CO–CO_2 atmosphere there is evidence
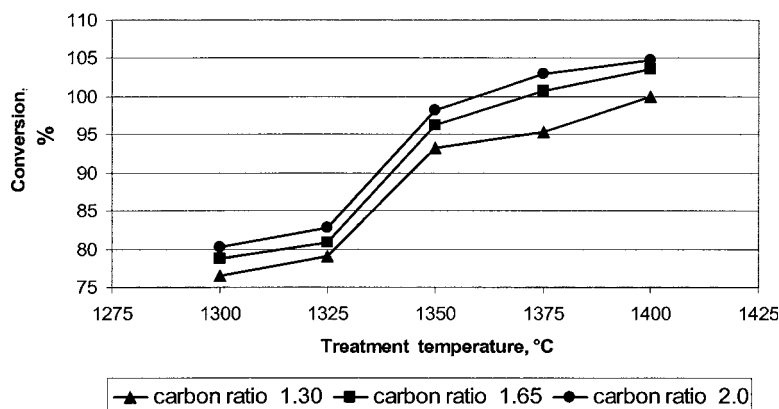
2 **Manganese ore reduction with temperature: weight loss data recalculated to give MnO to Mn conversion**

for the formation of Mn_2SiO_4 throughout the composition range.[8]

The other phenomenon is the formation of Mn_7C_3 (melting point 1340°C) as the carbon content in the manganese liquid increases. However, the carbides would be small and intimately mixed in the agglomerates and are unlikely to coalesce until the gangue phases melt. In Fig. 2, the mass loss data have been recalculated to give conversion levels of MnO to Mn.

For each set of conditions, the higher the coal rate in the manganese ore–coal–binder agglomerated blocks, the greater the reduction achieved. Because the treatment temperatures were about 40°C above the melting points, the blocks melted down. However, by selecting a slag modifier, it was possible to formulate a block that could withstand the elevated temperatures (Fig. 3). Deriving a block formulation that will give high levels of reduction without melting is important for materials handling.

CO₂ emissions

The tunnel kiln process has reduced projected CO_2 emission per unit of production as a result of the efficient use of coal in direct reduction as against the inefficient use of electricity in a smelter.

In a projected comparison for chromium production (Table 2), the electrical requirements during smelting were obtained from a study by a major plant supplier, estimated as the energy required for melting based on chemical analysis of the reduced product.[9] The electricity consumption is reduced from about 3400 kWh/t liquid alloy for the conventional route to about 2400 kWh/t for the tunnel kiln and smelter process.

The coal addition rate is shown for carbon ratios of 1·33 and 2 times stoichiometry. The carbon ratio of 1·33 is known from tests to provide metallisation >90% for chromium and a higher percentage for iron. The 2·0 ratio was examined to allow additional energy for heating requirements in kiln operation. The other carbon requirement in a smelting operation is for burden conductivity. However, until further test work has been completed, this carbon addition rate is uncertain.

In manganese operations, a similar argument could be constructed around the savings in electricity usage as against coal for direct reduction. Where sintering facilities are not available, the tunnel kiln offers advantages for calcining the burden, thus allowing better furnace control. An electricity saving >1 MWh/t of alloy is expected.

3 **Reduced manganese ore–coal+3% additive (slag modifier) block after treating at 1375°C for 6 h under carbon monoxide**

Table 2 **Projected mass of CO_2 produced in tunnel kiln and conventional process**

	Carbon ratio* 2·00		Carbon ratio* 1·33	
	t CO₂/t Cr metal	%	t CO₂/t Cr metal	%
Conventional route	11·7	100	11·7	100
Tunnel kiln				
Via smelter, no coke	9·7	83	8·5	73
Via smelter, with coke	11·3	97	10·2	87

*Relative to stoichiometric quantity for complete reduction.

Other operators are examining ways of reducing emissions. In Norway,[10] biocarbon sources are being examined as potential substitutes for fossil fuel, i.e. coal and cokes. This will allow a reduction in Norwegian ferroalloy CO_2 emissions from 3·0 to 2·5 Mt/year. However, the cost of biocarbon is about double that of fossil fuel.

The 1997 Kyoto Protocol requires signatories to reduce CO_2 emissions to 7% below 1990 levels between 2008 and 2012 and methods such as those outlined here could allow countries to achieve these targets.[11] As a developing country, South Africa is not subject to this limitation.

Alternative routes to stainless steel

The product leaving the tunnel kiln could be considered for use without having to be processed through a smelter. In the manufacture of stainless steel, a direct reduced chromium bearing product could have advantages as a direct charge feedstock. The tunnel kiln product would be about half the cost of a ferroalloy feed in terms of chromium units, due to elimination of the additional costs of a smelting unit. If a method could be found for melting out, e.g. hf induction, then a liquid supply that could be synchronised with the demands of the steelmaking unit would be available, leading to increased productivity.

Other routes are possible, e.g. one based on the VAI–Kawasaki concept.[12] At Chiba works in Japan, a cost saving stainless steelmaking process is in operation. Featuring two converters, this process is based on the smelting reduction of chromite ore in a bath of dephosphorised hot metal. The required process energy is generated through the combustion of coke additions and by partial post-combustion of the converter offgases. In a second converter step, the chromium alloyed hot metal is decarburised to high quality stainless steel.

Other ferroalloys

Another possibility would be the use of a Corex plant for the manufacture of an Fe–Mn alloy in which the manganese would be sourced from tunnel kiln product. This would allow the production of ferromanganese without the very high export gas volumes associated with a blast furnace type operation.
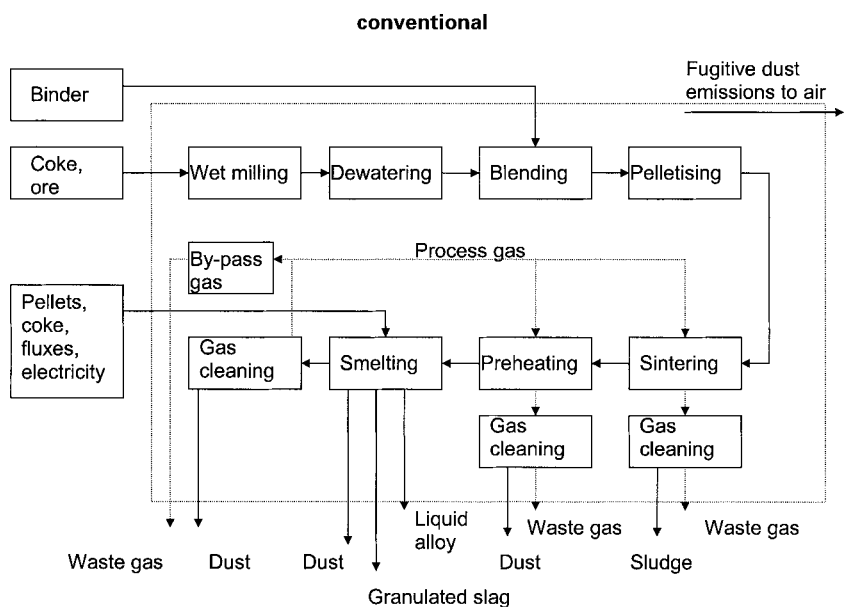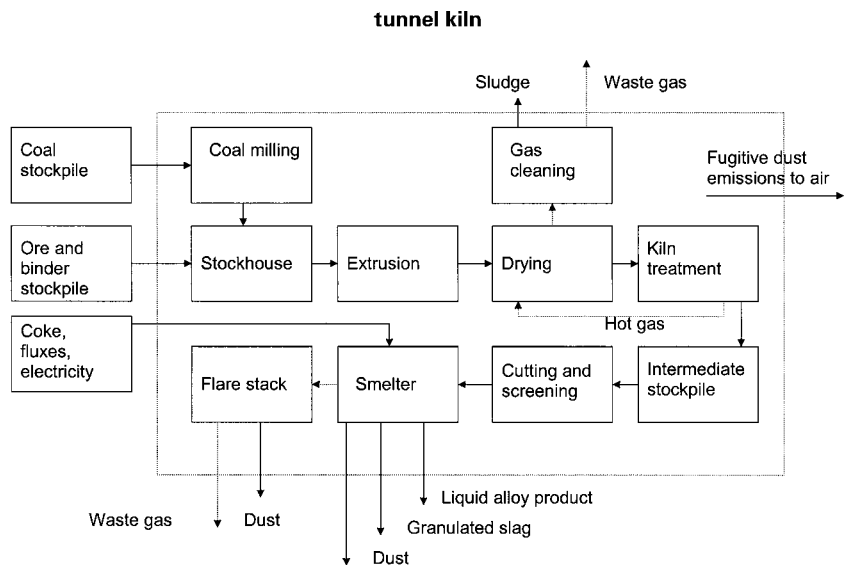
4 Flow charts for tunnel kiln process for direct reduction with conventional smelting equipment and standard process for pelletising and sintering with preheating before smelting

Life cycle analysis

Life cycle analysis (LCA) is a powerful tool for analysing true environmental impact. The analyst can determine which materials or processes dominate the environmental impact of a product, allowing a focused search for environmentally sound options. The analysis carried out here uses the most up-to-date LCA information and techniques available.

In the South African ferrochrome industry, the most popular process for handling fine chromite is pelletising and sintering. Chromite ore is finely milled and blended with a small amount of coke, sintered under oxidising conditions and finally reduced in a conventional submerged arc furnace.

In the manganese industry, there is no clearly preferred route for handling fine ore, although sinter plants are being considered, and for low grade titanium slag recovery there is currently no well developed alternative for comparison. The LCA was therefore restricted to a comparison with the sinter plant route used in the ferrochrome industry.

The same battery limits are assumed for both routes, i.e. raw materials stockyard to liquid ferrochrome in the ladle. This omits, on the one hand, the mining processes and, on the other, handling of the liquid product, i.e.
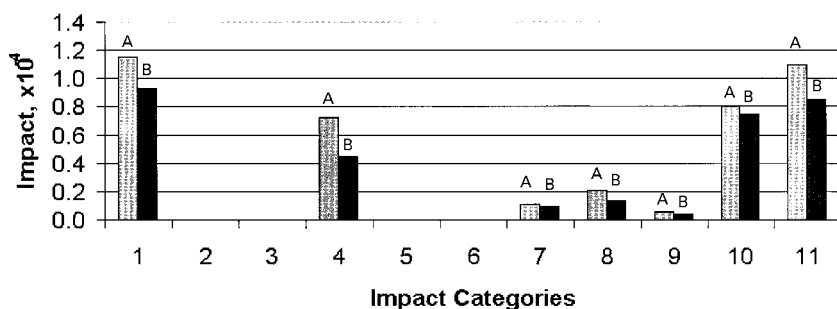
1 HH carcinogen respirable; 4 HH climate change; 7 EQ toxicity; 8 EQ acidification – eutrophication; 9 EQ land use; 10 R minerals; 11 R fossil fuels

5 **Comparison of environmental impact of tunnel kiln (B) and conventional pelletising and sintering process (A): normalised impact, excluding dust**

casting, crushing and sorting. The production routes are shown schematically in Fig. 4.

Apart from physical differences in plant layout, the processes differ in energy consumption. The tunnel kiln process uses raw coal for reduction (716 kg/t liquid metal) and electrical energy (2400 kWh/t) for final melting. As a consequence of the prereduction step, the electricity requirement at the smelter stage is reduced. In addition, some carbon in the form of coal or coke (20 kg/t) is required during final melting to satisfy the reduction of residual oxides.

The standard process uses electricity (3400 kWh/t) for smelting and a large component of coke (546 kg/t) as reductant and to achieve electrical conductivity in the burden. The energy for sintering is derived from smelter offgases and from coke blended into the pellet mixture.

The impact assessment phase of the LCA study was done using the Eco-indicator 99 H/A method of Pré Consultants,[13] modified to include the resource impact of using South African coal for electricity generation. In a procedure called 'characterisation', the method groups all inputs to the life cycle system from natural resources and all emissions to air, water and soil into 11 impact categories. The results are then normalised by comparison with a reference system, the existing impact of the European background levels. A weighted average single score for the entire life cycle system is obtained using weighting of 400 for human health and ecosystem quality and 200 for resources.

Potentially significant sources of uncertainty in these procedures have been discussed by Ross.[14] In the present study, the uncertainty has been reduced by using data for local South African electricity production, to improve the quality of the data and to

make it more site-specific. Sensitivity analysis was not carried out because of the lack of sufficient spatial, temporal, dose response and threshold information to estimate variance.

LCA results

Dust arising from both processes was found to be the most important factor affecting environmental impact. However, no data or design constraint could be identified to show that either process would produce more dust. The effect of dust was therefore omitted from the comparison.

Results of the normalised comparison are shown in Fig. 5. The main environmental impacts are shown in four categories: under the Human Health (HH) grouping (carcinogens and climate change) and under the Resources (R) grouping (minerals and fossil fuels). The resources impact is an anticipated consequence of raw material consumption during processing because of expected higher metallic yields. Under the HH-grouping, the impact on climate change is due to CO_2 gas evolution during electricity generation and carbon usage for reduction. The impact on the carcinogen category can to a large extent be ascribed to electricity generation from fossil fuels, since some chemicals produced during electricity generation can be carcinogenic.

In the mass and energy balance calculations, it was assumed that the chromite feeds for both processes are high grade fines. The lower impact for the tunnel kiln process results from the higher anticipated chromium recovery. If, however, it is assumed that more of the discard UG2 seam chromite from platinum mining can be used in the tunnel kiln than in the standard process, the former will be even more favourable in minerals resource impact. A reduced effect is observed under the

grouping for ecosystem quality and again this is ascribed almost entirely to electricity generation from fossil fuels.

Because the impacts are additive, it can be seen that the environmental effect of the tunnel kiln is less than that of the standard route. For the HH category it is about 28%, for the EQ category about 23% and for the R category about 16% lower.

Conclusions

The proposed tunnel kiln technology has potential applications for:

- direct reduction of chromite in the manufacture of cheaper ferrochromium
- direct production of stainless steel from highly reduced chromite
- direct reduction of manganese in the manufacture of cheaper ferromanganese
- production of crude ferrosilicon
- direct reduction of iron ore fines (especially magnetite fines) that could then be charged to a blast furnace
- direct reduction of in-plant waste oxide materials for recycling, adding to plant productivity
- nitriding of titanium bearing slags and minerals for the recovery of TiO_2
- reduction of sulphates (e.g. precipitated barium sulphate).

Its advantages include:

- ability to process fine particulates, allowing use of ore fines generated during mining
- can handle materials that soften and become sticky under high temperature processing
- allows use of coal to reduce or eliminate coke requirements
- reduces electricity requirement for smelting (from 3400 to 2400 kWh/t of chargechrome in ferrochromium production)
- projected as more economical than alternatives, especially when using low grade minerals such as UG2 discards from the platinum industry, where high metal recoveries are essential to produce a product of acceptable quality
- reduces CO_2 emissions (for ferrochromium by about 20% per ton of liquid metal)
- higher metal recoveries
- avoids the need for hot briquetting when reducing iron ore fines.

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