Refining of charge chrome: a study of some products and applications

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Synopsis

By implementing a converter downstream of the reduction furnace it is possible to broaden the product range significantly. The converter can also successfully be used to strip furnace slag from chromium oxide. Some process alternatives and their economical, practical and environmental implications are studied using process models developed based on UHT's long experience in stainless steelmaking, stainless steel process control and charge chrome refining.

Keywords
Charge chrome, converter refining, ferrochromium products, process design.

Introduction

In this document the process for refining charge chrome with the objective of making MC FeCr and some other refined charge chrome products is described. Such a process has been operated by Samancor Chrome in Witbank since 1986[1]. That process and plant were designed by UHT AB. Recently there has been a renewed interest in this process and in similar process alternatives with slightly different objectives in mind.

This paper serves to describe how the converter operates, how the process can be simulated, and some important product types and process advantages that might be achieved by the refining. Some of the products described in this paper are very tough and cannot be crushed with normal ferroalloy practice. In these cases it is suggested that these products are granulated. The granulation using the GRANSHOT® method is part of the charge chrome refining process taking place in Witbank.

Theory on converter metallurgy in high chromium systems

The converter plant

The converter plant is a relatively simple and low capital plant compared to other pyro-metallurgical units such as furnaces or kilns. The main components are: gas farm, valve station, raw material distribution centre, converter vessel with tilting machinery, wrecking and relining stations, water cooled off-gas hood, ducting, gas coolers, and fume treatment plant. The vessel is placed in a building where an overhead crane can enter with hot metal from furnaces, where treated metal can be taken to casting, and where the converter vessel can be lifted between wrecking, relining and operating positions. A schematic converter plant is displayed in Figure 1; the approximate footprint of that particular configuration is about 24 by 36 metres.

Due to difficulties associated with transporting and storing of liquid charge chrome for long periods, it is necessary to have the converter reasonably close to the metal supply. Charging within approximately 30 minutes after tapping of the furnace is desired to avoid skulling in the ladle or solid slag closing the ladle spout and creating ladle tapping/converter charging difficulties. In most applications the converter process is fast compared to the reduction furnace so it is relatively easy to design the converter to match the tapping cycle of several furnaces.

Fundamentals of charge chrome refining

Some important reactions in this system are the ones discussed in Table I. Metallurgy involving phosphorus, sulphur and nitrogen are discussed separately in the text.

During the refining oxygen is blown and silicon is initially removed together with the titanium and aluminium that might be present. These reactions are all favoured by a low temperature. Once the temperature has

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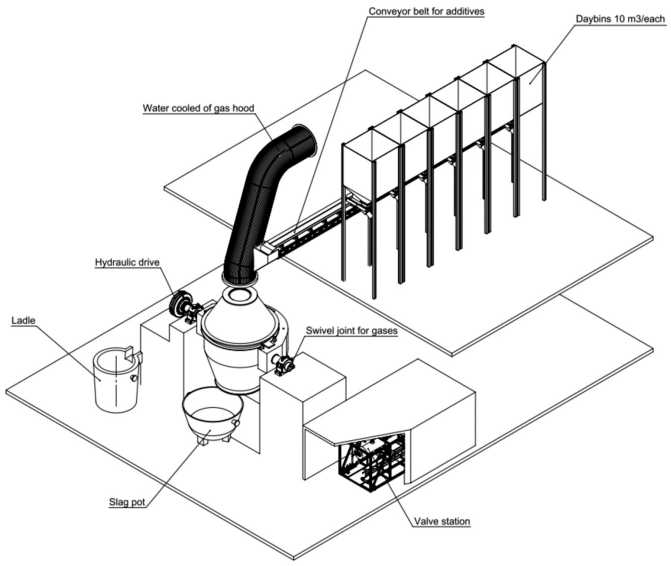

Figure 1—Schematic plant layout for plant suitable for charge chrome refining

Table I

Important reactions in charge chrome oxygen refining

Reaction	No.	Comment
$\underline{C} + ½\ O_2 \Rightarrow CO$	1	Main source of carbon removal (weak exothermic)
$2\underline{Cr} + 3/2\ O_2 \Rightarrow Cr_2O_3$	2	Main source of chrome oxidation (strong exothermic)
$3\underline{C} + Cr_2O_3 \Rightarrow 2\underline{Cr} + 3CO$	1–2	This strong endothermic reaction does not occur to an important extent, yet it represents the basic process very well. High temperature, carbon and chromium oxide activity together with low activity of chromium as well as low partial pressure for carbon monoxide favours decarburization. For practical purposes this means that more inert gas has to be added to remove carbonmonoxide the lower the carbon content becomes.
$\underline{Si} + O_2 \Rightarrow SiO_2$	4	Source of Si removal (strong exothermic)
$H_2O \Rightarrow H2 + ½\ O_2$	5	Steam is supplied to balance excess heat in the converter. Free hydrogen will substitute argon and nitrogen and simultaneously add oxygen.
$\underline{Ti} + O_2 \Rightarrow TiO_2$	6	Source of Ti removal (strong exothermic)
$2\underline{Al} + 3/2\ O_2 \Rightarrow Al_2O_3$	7	Main source of aluminium oxidation (strong exothermic)
$\underline{Si} + 2/3\ Cr_2O_3 \Rightarrow SiO_2 + 4/3\underline{Cr}$	4-2	This weak exothermic reaction represents the chromium oxide reduction from the slag

increased sufficiently the decarburization becomes the dominant reaction and carbon monoxide will form from most oxygen added to the hot metal. Initially the rate of oxygen supply limits the process; see Figure 2.

The gas blowing is done through combinations of submerged annular tuyeres, top-tuyeres or through a water cooled lance system in larger converters; see Figure 3. The oxygen comes mainly from two sources: oxygen gas or superheated steam produced on site.

At lower carbon activities chromium oxidation is the dominant reaction in the converter unless measures are taken to lower the partial pressure of the formed carbon monoxide. This is done by injection of inert gas.

During the carbon removal period the temperature must be controlled to ensure that it is neither too low so chromium is oxidized nor too high to prevent excessive lining wear. Experience has shown that a temperature slightly above 1700°C is the optimum. This temperature coincides with what is normally used in stainless steel refining.

This metallurgical oxidation process is characterized by a significant energy surplus, raising the temperature when carbon, chrome or silicon oxidize. Balancing of the temperature at an optimum level demands active measures to be taken, either to dilute the energy with more mass, to use energy consuming reactions, or to remove the heat to the off-gas by inert gas purging.

The possibility of diluting energy with more mass is limited. It is possible to use crushed charge chrome at high carbon levels but at lower carbon levels this is inefficient. At this stage of the process it is more efficient to dilute the energy by using fines of the final product or mild steel scrap. However, the mild steel scrap not only dilutes the energy but also the composition, resulting in a product with lower chromium content.

There is a resistance to dilute chromium with iron as a high Cr/Fe ratio traditionally has ensured a higher product value and lower transport costs. This tradition may remain strong but, for instance, FeNi users have accepted that the well defined iron units have a value.

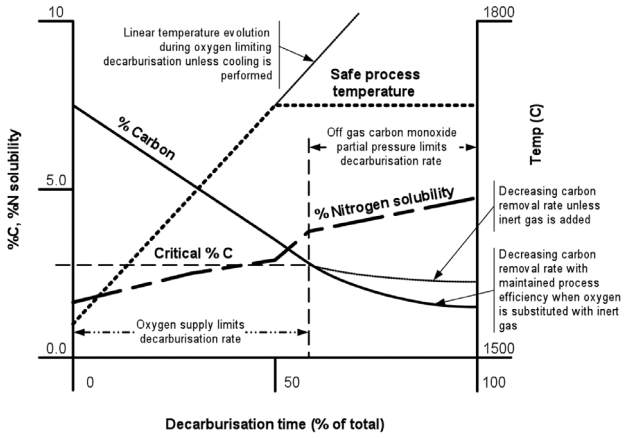

Figure 2—Schematic process limitations during different stages of the decarburization

The strategy of using energy-consuming reactions for temperature control in the converter is the most practical process approach in terms of time, economy and environmental impact. Several reactions are possible to rely on. To use silicon transferred from the furnace to reduce slag from the previous heat, will remove most heat which otherwise would be generated by oxidation of silicon by oxygen gas. This method is used in the UHT process for IC3 production. Later during the decarburization process superheated steam is a very attractive alternative to balance the temperature. It has no negative effects on the process and will actually lower the total production cost.

The steam adds oxygen and necessary inert gas for lowering the carbon monoxides partial pressure while consuming energy via the reduction of steam into oxygen and hydrogen; see reaction 5 in Table I. A particular advantage of steam is that it substitutes argon as inert gas for partial pressure reduction. The steam cost is only a fraction of the argon costs on most markets and it is produced on demand without big investments in air distillation plants.

The reason why steam or argon has to be used as inert gas in this production rather than the more available and cheaper nitrogen is that nitrogen dissolves easily in the refined chromium product that has high nitrogen solubility; see Figure 2. High nitrogen content is undesirable in most applications.

It is not possible to remove phosphorus in the refining stage. Its affinity to oxygen is too low compared to that of chromium's so separation is not feasible in a traditional oxidizing refining process. Sulphur removal, on the other hand is very efficient and occur spontaneously as a consequence of refractory protection if the oxygen potential is lowered in the metal just prior to tapping it.

For the slag, metallurgy is done in the Cr_2O_3-SiO_2-CaO-MgO-system. The main idea is to work with a solid Cr_2O_3-rich slag during decarburization and to reduce Cr_2O_3 in this slag using Si after the decarburization. This reduction will melt the slag and create a liquid slag suitable to decant. The fluid reduced slag will be aggressive to most common refractory if a high basicity is not maintained. A high basicity also promotes the silicon's ability to reduce Cr_2O_3 from the slag[4]. High MgO content enables suitable refractory as magnesia, chrome-magnesia or dolomite to resist chemical attack from the slag.

Process model used for simulations

General

UTCAS is an advanced computer system specially designed for converter process management. The system concept includes an effective real-time process control system as well as tools for process design and production evaluation; see

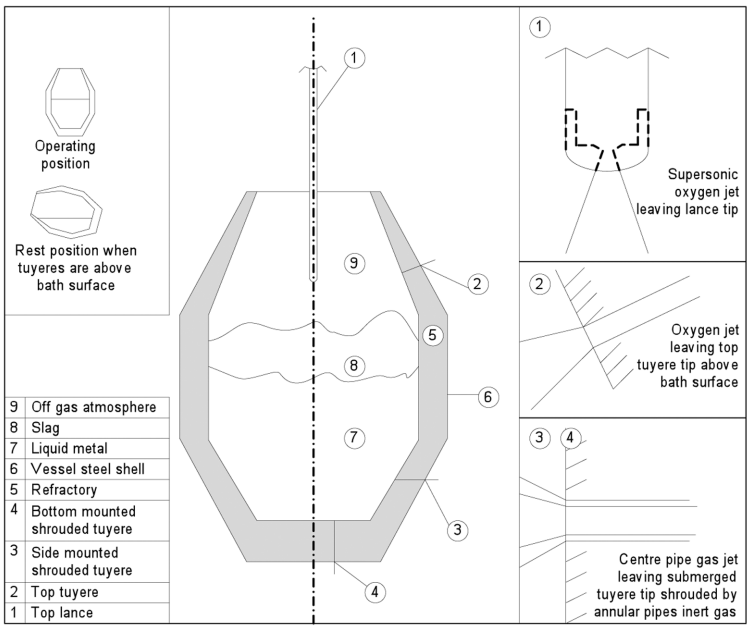

Figure 3—Different means of gas introduction to the converter process

Figure 4. It is used for stainless steelmaking in Outokumpus Avesta Works as well as in Acerinox's Columbus Stainless Works, it has also been used for production of a number of different refined ferrochrome products at Thos Begbie's foundry in South Africa.

Process design

The processdesign tool provides an environment for designing tailor-made process routes. The total process is built up of different steps with different properties for controlling the utilization and distribution of gases and materials. The steps are put together into sequences in various combinations representing the most suitable practice for processing each grade. In addition to the step sequence, the process targets and the presumptive start conditions are defined with respect to chemical composition, mass and temperature.

The practice serves as a framework for the process optimization function, which is the main mathematical model. It is able to optimize the exact amounts of gases and materials in order to move from the given start conditions to the defined targets in the most economical way for the rules and limitations set by the step sequence definitions. The metallurgical core model is based on Sjöberg's work[4].

The optimization model is able to control and balance the temperature by means of:

- Adjusting gas mixes (oxygen/inert ratio) over time
- Distribution of calculated amounts of alloys and slag formers
- Determining amounts and distribution of additional cooling additions.

By combining these functions, the process optimization finds solutions to control both overall and local energy surplus generated as a consequence of the strategically defined practice.

Processing

When a heat is processed, a suitable practice for the planned grade is automatically selected from the database. The real-time process control system executes a process optimization and eventually UTCAS initiates gas blowing, material weighing and addition according to the optimized process plan by giving set points to the PLC.

The process is run fully automatically until UTCAS or the operator detects a deviation from the expected results, which causes the process plan to be re-optimized and changed.

Some product alternatives

Some products

Based on liquid charge chrome, it is possible to make a number of different products with access to a converter; these are illustrated in Figures 5 and 6. The products are analysed throughout this section.

Downstream process reasons to use different products

In most cases the metal value increases as the concentration of C and Si decrease. At the same time, however, the operating costs for reduction and possibly refining increase and the metal becomes more difficult to refine at acceptable temperatures.

There is a general desire from most producers to make a product as high in chrome as possible as it is cheaper to transport this product and it is undesirable to spend expensive reduction agents on iron reduction. But for the user low chromium products can be just as attractive as the refined iron in the product has a significant value.

A lower chrome content lowers the liquidus temperature and makes melting, liquid storage and transporting cheaper and easier. Lower chrome in solid products means that refined iron units are available in a shape suitable for automatic handling.

Silicon in stainless steelmaking

When silicon is added to the EAF in a steel melt shop it may be consumed by oxygen from air or injected oxygen gas, or it may be consumed by oxides present in the slag, or oxides charged to the furnace with the metal. When the silicon is oxidized in the EAF the formed silica has to be bound to lime

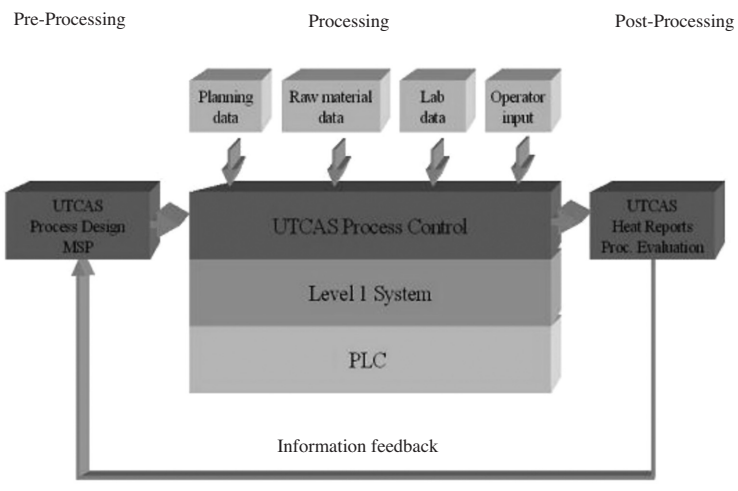

Figure 4—The UTCAS concept for process control and management[3]

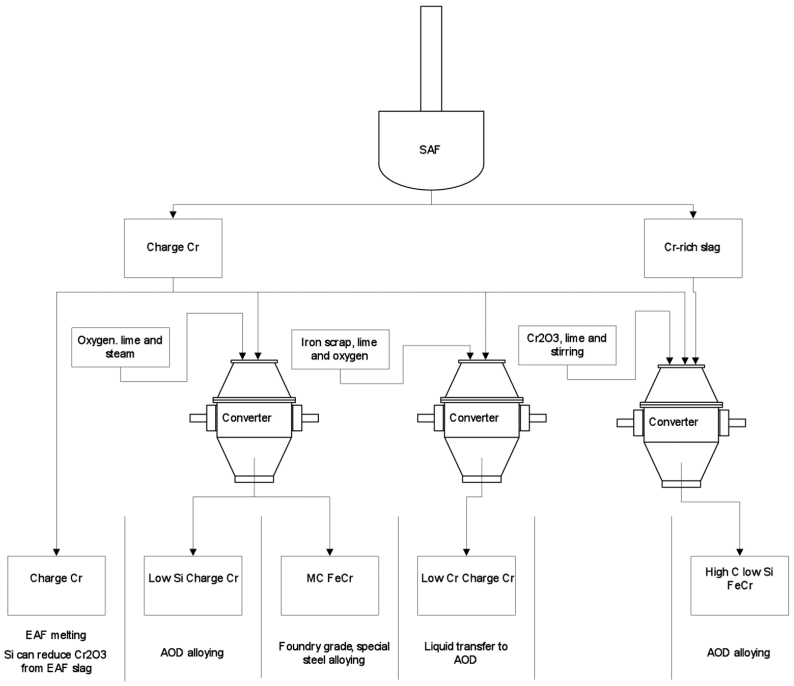

Figure 5—Process routes and products; reactors and reagents

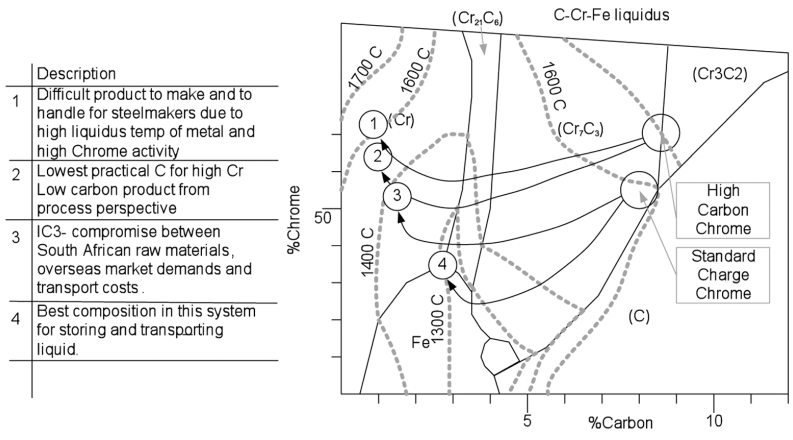

Figure 6—Process routes and products; metallurgical routes and merits, phase diagram according to Rao[5]

and magnesia to make it harmless to the refractory. In the relatively low working temperature in the EAF this means a CaO/SiO_2 ratio around 1.1–1.5. This means that relatively little slag is generated as a function of the formed silica in the EAF-of course even less silica would have formed without the addition but due to air leakage some silicon will be necessary to limit chromium losses, and some of the silicon added may actually reclaim chrome from the slag.

The silicon that is carried over to the converter or that is added to the converter with the charge chrome will exclusively be consumed by oxygen blown with the purpose of decarburizing. This means that it prolongs blowing time while it adds slag to the system at an early stage of the process; this again means that more chromium is trapped in the slag at the same activity situation and that more silicon will be necessary to reclaim the chromium at a later stage—the process enters a vicious circle. The necessary CaO/SiO_2 ratio in the converter is generally 1.8 to ensure a lime saturated slag at the temperatures necessary to operate the process; this means more slag is necessary in the converter than in the EAF for each charge chrome unit used.

The silicon carried over is slightly less problematic than the silicon added during the process due to the possibility of removing it selectively by oxidation at a relatively low temperature.

The conclusion from this is that silicon added to the EAF with charge chrome is harmful to an extent but beneficial to an extent, whereas silicon added to the converter with the charge chrome is only harmful. Thus the traditional charge chrome composition is better suited for the EAF than for the converter. Some chrome alloying is, however, necessary in the converter so alternative chrome products are necessary.

Refining of charge chrome: a study of some products and applications

Customer value of different products

The charge chrome's main merits are that it is easy to produce, it is well known on the market, and it is acceptable for melting in electric arc furnaces where crude stainless steel is produced. Some alternative products based on charge chrome are presented in Table II. The processing of these products is demonstrated in Figure 7 where a 40 t heat with 54%Cr, 7.5%C, and 3% Si charged to the converter at 1550°C have been simulated using UTCAS software,

Low silicon charge chrome, where silicon has been selectively removed, is a good product for stainless steelmaking. The lack of silicon makes it particularly suitable for the AOD as much lower slag volumes and lower consumption figures are obtained when using it. The low silicon charge chrome also has lowered of S and Ti contents. As seen in Figure 7, top left graph, the silicon removal is fast, and it is done by blowing a mixture of steam and oxygen that maintains a low temperature in the metal while sufficient oxygen is added to oxidize the silicon.

Medium carbon ferrochromium is the next refining stage; the product is of interest mainly in foundry industry and in special steelmaking plants where refining capacity is limited and where a premium is paid for low Si as it enables efficient aluminium deoxidation of the products with maintained silicon control. In Figure 7 this process is demonstrated in the second and third row to the left—in the lower case a top lance is used which makes that case slightly faster. Initially carbon is removed to the desired level while some Cr also oxidizes and becomes trapped in the slag.

During the carbon removal, oxygen and steam are mixed to maintain a suitable temperature and sufficient inert gas to create optimum decarburizing conditions—this means more steam at lower carbon content. The metal is then tapped while slag is kept in the converter. When metal containing slag transferred from the reduction furnace on the next refining cycle is stirred together with the old slag, the Cr from the slag is reclaimed and the liquid Cr free slag can be decanted. This is both a very fast and environmentally attractive way of using the silicon.

Table II

Some refined charge chrome compositions and amounts after different treatment

Product	Weight (kg)	%C	%Cr	%Si	%Fe	Shape	Comment
Charge chrome	1000	7.5	54.0	3.0	34.5	Lump	Product for reducing EAF practice
Low Si charge chrome	965	7.8	56.0	0.5	35.8	Lump	Good product for stainless steelmaking
MC FeCr	903	1.4	59.8	0.6	38.2	Gran	Product suitable for foundry and special steel
Low Cr MC FeCr	1430	1.4	37.8	0.3	60.5	Liq	Suitable for liquid transfer and storage
High Cr low Si charge chrome (start %Si=6.0)	1099	6.8	62.7	0.5	33.2	Lump	Excellent product for stainless steelmaking

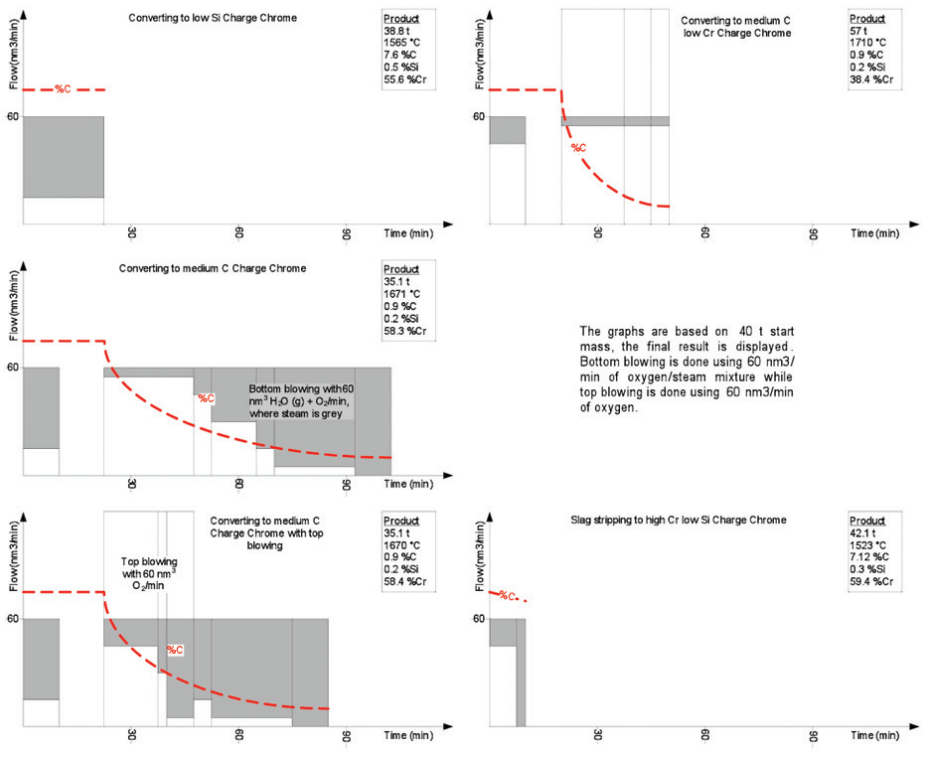

Figure 7—Graphical representation of production process to make the different products suggested. The graphs display how gases are introduced in the process during different time frames to obtain different products

Table III

Production cost estimation for different grades

Source	USD/kg	USD/nm^3	USD/h	L Si ChCr	MC FeCr*	MC ChCr **	L Cr ChCr	H C L Si ChCr
ChCr	1,2 ***	(100 c/lbs)		48000	48000	48000	48000	48000
Fe-scrap	0,25			0	0	0	5000	0
FeSi	1,2			0	0	0	0	0
Oxygen		0,1		33	235	231	338	43
Steam		0,05		50	153	160	15	7
Slagformers	0,1			480	480	480	360	1200
Time incl. refractory	600	330	1010	830	490	390		
Production cost at 98% Cr-yield (USD)				49872	50857	50680	55182	50620
Produced amount (kg metal)				39026	34931	35045	56667	42137
%Cr				56	59,8	59,8	37,8	57,5
c/lbs				104	111	109	117	95

Costs are based on estimates and costs from asianmetal.com[6]
*MC FeCr produced without top lance
**MC FeCr produced with a top lance
***the price for ChCr in the calculations is FOB prices of crushed material which is much higher than the actual figure for liquid charge chrome

Low Cr medium carbon ferrochrome is an alternative to medium carbon ferrochromium if there is a premium for the iron units in it after dilution of energy and chromium concentration. In cases where liquid transfer to a melt-shop is expected, this is a very attractive product as the lower liquidus temperature makes the metal much more transportable with a low risk for skulling, little refractory erosion and even simplicity in containing the metal in a holding furnace. For the receiver of the metal this product means possibilities to dephosphorize the EAF melt as well as obvious savings in energy for Cr and Fe units that are transferred liquid. In Figure 7 this process is demonstrated in the top right-hand graph. This process consumes surplus energy on melting in scrap. The added scrap dilutes the Cr content.

High Cr low silicon charge chrome is made slightly differently from the other alternatives and ideally requires higher start silicon content, in the range of 5–7%. With 6% Si a 60% Cr high carbon low silicon grade is made if furnace slag rich in Cr and metal is mixed in a converter. This product is very well suited to stainless steelmaking but it is also environmentally attractive as the silicon has been used to strip the furnace slag from chromium oxide. In the lower right case of Figure 7, furnace slag is charged on the high silicon charge chrome and the gas blowing is used to mix the phases well, thereby reducing Cr from the slag using the metal's silicon.

In Table III some basic economic figures for these scenarios are displayed when 98% yield is estimated for the Cr in the converter process. As seen in Table III, the cheapest Cr product to produce is the one where furnace slag is stripped using transferred silicon. The price difference between the different grades need, however, not be significant based on these figures, and all the products can easily be motivated in different applications by different markets.

Conclusions

To be able to provide the market with a range of charge chrome alloys suitable for different purposes, a converter is a valuable tool.

UHT's converter automation system UTCAS is valuable in process development to design the correct process and to evaluate its feasibility. It is also useful for evaluating the potential of different alloys in stainless steelmaking.

The silicon in the charge chrome may be beneficial or be costly for the clients. This is important for the charge chrome makers and traders to understand in order to maximize the product value. By using the correct charge chrome alloy in each situation, substantial benefits are obtainable for charge chrome users. These benefits are economic, technical and environmental.

To be able to see iron as a valuable product rather than a cost will be an important challenge for ferroalloy producers and traders in the process of broadening the product range.

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