REFINING OF FERROALLOYS WITH THE CLU® PROCESS

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ABSTRACT

With the growing consumption of more high-strength and demanding steels the requirements from the steel producers for refined ferroalloys are increasing. The key is the CLU® converter refining process, where superheated steam decomposes into hydrogen and oxygen while consuming heat. No electrical power input is required. With the CLU process a wide range of refined ferroalloys can be produced cost-effectively.

The CLU process is ideal for medium carbon ferrochrome and ferromanganese due to the excellent temperature control. In manganese production this proves to be an extra valuable feature since temperature control is vital in order to minimise the manganese vaporisation.

By the use of advanced process control systems the refining is optimised for each situation. This paper discusses the fundamentals of refining of ferrochrome and ferromanganese and the benefits obtained through the CLU converter refining process. UHT's process control system UTCAS®, specially designed and developed for refining processes, is also discussed.

1 INTRODUCTION

In 2011 the world production of Mn and Cr was about 20 million ton together. Out of this less than 10% of the Cr was refined while more than 70% of the Mn was lower carbon-containing products other than HC FeMn. This difference is primarily caused by Cr being added as a bulk material in melting furnaces for stainless steel production while Mn is mainly used in secondary metallurgy in mild steel production. For stainless steel the amount of steel on the market has increased tremendously, however the type of steel in demand has not changed dramatically.On the mild steel side the high strength steels with low alloy amounts has been one of the fastest growing segments. These high strength steels tend to combine low carbon, high manganese and moderate silicon levels causing a mixture of SiMn and MC FeMn to be the most cost effective alloy mix. Between 2001 and 2011 the amount of refined FeMn consumed increased by 2.4 times.

For Mn the historical market development shows that products with low carbon content are gradually becoming more attractive. Due to increasing demand for steels with higher strength-to-weight ratio this development is likely to continue. With a FeMn-converter it is possible to remove carbon down to less than 0.5%C at a reasonable cost.

Most of the big Cr consumers can use any source of FeCr. Due to this they have focused their attention on getting hold of the bulk of the Cr at a low price. The bulk of the Cr is however not all the Cr and even in the bulk segment there is room for improvement and niche strategies. From 2001 to 2011 the Cr-production rose by 2.5 times but the refined products only increased by about 10%. Currently LC FeCr with 0.1%C is about twice as expensive as HC FeCr while 2%C FeCr is 1.5 times as expensive per Cr unit, see Table 1. To increase the refined FeCr segment it will be necessary to find more cost-effective production solutions and to prove the benefits of refined products to the users to be able to increase the portion of refined Cr in the market.

Most of the refined FeCr produced today is made using a silicothermic process; however, some is already made by oxygen steelmaking methods. FeCr with carbon content down to 0.1% can be made in the CLU-process but more importantly bulk FeCr with better steelmaking properties can also be made. With a better product that delivers the same amount of Cr-units but that adds less cost for the producer it is probable that consumers are willing to pay a premium.

By utilizing the chemical energy that is available in HC FeCr in the form of Si and C for remelting of fines that will otherwise be discounted and by reducing Cr-ore in the process, the process cost for the refining can be kept low. At the same time, a product can be made that gives advantages in the steelmaking in the form of lower melting temperature, less need for refining and a more mechanically stable raw material.

Table 2: Production and prices of Cr and Mn alloys

	Chromium		Manganese	
	Produced Cr 2012	5120 kT	Produced Mn 2012**	13000 kT
	Estimated refined amount	5-10 %	Estimated refined amount	8-10 %
	Cr-market increase (2002-2012)	100 %	Mn-market increase (2002-2012)	110 %
	Cr grade	**Price ¢/lbs**	**Mn grade**	**Price ¢/lbs**
	ULC FeCr 0.05% C	246	Mn metal	150
Possible products fromCLU process	LC FeCr 0.1%C	228	LC FeMn 0.1% C*	127
	LC FeCr 0.15%C	219	-	
	LC FeCr 0.5%C *	202	LC FeMn 0.5% C*	111
	LC FeCr 1.0%C *	187	MC FeMn 1.0% C*	99
	MC FeCr 2.0%C *	167	MC FeMn 2.0% C	91
	MC FeCr 4.0%C *	135	-	
	HC FeCr 49-51 %Cr	115	HC FeMn 78% Mn***	72
	HC FeCr 60-65 %Cr	122	SiMn	63
	* Estimated price based on quoted prices [1],[2] ** Estimated production based on quoted production [3] *** Recalculated to a 78%Mn base from quoted price [2]			

2 FUTURE DEMAND FOR REFINED FECR AND FEMN

The authors believe there is a need for some refined Cr-products that does not currently exist.
Some of these have also been discussed by the authors in previous papers [4-6].

Undereutectic low liquidus FeCr with 3-4 %C and low Si-content. This product can be made very efficiently and cheaply by balancing the furnace Si-content with Cr-ore and by a gentle carbon removal at low temperature. The product is excellent melting stock in electric furnaces as its low melting temperature decreases the necessary tap temperature and save melting time, energy and refractory. The product is also suitable for producers that base their production on Nickel Pig Iron that naturally has high content of C and Si that has to be removed during the stainless steel refining. The product does well as a melting stock for VOD-operators who can only handle limited C and Si in their process. Finally, this product is a very good alloy/coolant to use in AOD's. Figure 1 shows a FeCr product in granulated form.

Figure 1: Granulated FeCr product.

Low-carbon FeCr made in the converter route. This is a challenging product where much slag is generated. Nevertheless, it will be a very cost-efficient alternative to LC FeCr made by the silicothermic route. Traditionally, low-carbon FeCr prices are two to three times as expensive as HC FeCr products. With a production cost increase of 70%

compared to HC FeCr, price could be lowered for LC FeCr and this could alter the demand situation for this grade dramatically.

Furthermore, the authors believe that there will be an increasing demand for **medium- and low-carbon FeMn** both inside and outside of China during the next 10 years. The demand that is necessary to satisfy the market could be double to or even greater than what is presently available. The furnace capacity is largely present already but the refining capacity is lacking. The refined FeMn will have to compete with EMM and SiMn. It will be essential for this niche to ensure that only ores and coke with low phosphorous content is used to make the product a good alternative to EMM.

A potential niche that is less studied is to purposely add **nitrogen in the LC FeMn** during the processing. Many of the steels that have a high Mn concentration also have high nitrogen content. As Mn is added late in the steelmaking process, introduction of Mn is not a simple task, nitrogen alloyed LC FeMn with acceptable price would be an interesting alternative for these applications.

3 CLU® PROCESS FOR REFINING OF FERROALLOYS

The CLU converter refining process makes use of superheated steam along with compressed air, oxygen, nitrogen and argon as bottom-blown process gas and oxygen as a top-blown gas. At elevated temperatures steam decomposes, in an endothermic reaction, into hydrogen and oxygen which are used in the refining process to achieve important process benefits. No electrical power input is necessary.

The CLU process is ideal for medium carbon ferrochrome and ferromanganese production due to the excellent temperature control without alloy dilution. In manganese production this proves to be a valuable feature since temperature control is vital in order to minimise manganese vaporisation. The CLU process also enables a broader production range with further refined products such as low carbon ferrochrome or ferromanganese.

In this section the benefits of using steam and the fundamentals of FeMn and FeCr refining are discussed.

3.1 Use of superheated steam as additional process gas

When superheated steam is introduced into the converter, it decomposes into oxygen and hydrogen according to equation (1). The formed hydrogen gas acts as an inert gas to replace argon while the oxygen takes part in the carbon oxidation process.

$$H_2O\ (g) = H_2\ (g) + \tfrac{1}{2}\ O_2\ (g) \qquad \Delta H = +\ 241.9\ \text{kJ/mol} \qquad (1)$$

Since the reduction of steam (eq. 1) is an endothermic reaction, i.e. consumes heat, an additional cooling benefit is obtained in the CLU process compared to alternative oxygen refining processes that requires cooling with scrap metal. By controlling the rate of steam blown into the converter, the metal temperature is balanced and the need for cooling material in the form of refined alloys or processed scrap is decreased. 1 kg of steam replaces 10 kg of coolant material.

As the transfer mass from the upstream reduction furnaces that produces the unrefined liquid metal varies from tap to tap, the CLU process gives a more flexible overall refining, where solid material and steam is optimised to reduce cost and increase productivity by enabling a flexible arriving mass and a fixed final mass. The advantage of improved temperature control and reduced refractory contact time also leads to lower refractory wear.

3.2 Fundamentals of FeMn refining

Production of MC FeMn and LC FeMn by decarburization of HC FeMn is a metallurgical challenge due to the low oxygen potential and high vapour pressure of Mn. To reach carbon levels below 2%, decarburization has to be performed at high temperatures.

The most important reactions to describe the decarburization process are:

$$\underline{C} + \tfrac{1}{2}\ O_2\ (g) = CO\ (g) \qquad (2)$$

$$\underline{Mn} + \tfrac{1}{2}\ O_2\ (g) = MnO\ (slag) \qquad (3)$$

The sum reaction is expressed as:

$$\underline{C} + MnO\ (slag) = \underline{Mn} + CO\ (g) \qquad (4)$$

$$K_4 = \left(\frac{a_{Mn} x P_{CO}}{a_{MnO}\, x\, a_C}\right)$$

Where K_4 is the equilibrium constant for reaction (4).

Also important is the effect of the Mn evaporation:

$$Mn\ (l) = Mn\ (g) \qquad (5)$$

The carbon removal is favoured by:

- a high temperature
- a high activity of C in the metal
- a low partial pressure of CO
- a low activity of Mn in the metal
- a high activity of MnO in the slag

For practical reasons the only parameter that can be controlled is the partial pressure of CO, Pco.

When the decarburisation starts the carbon activity is normally very high. Added oxygen is mainly consumed by CO formation. The MnO formation increases gradually as the carbon content decreases. The formation of MnO, along with the formation of CO, are exothermic reactions generating heat in the process.

To avoid too high temperatures cooling is necessary. The cooling can occur spontaneously by manganese evaporation according to reaction (5), however this is costly as it decreases the yield. Cooling can be done by recycling refined FeMn but this lowers the yield and increases the treatment costs. Finally the cooling can be done by utilizing endothermic reactions such as the reduction of steam.

In Figure 2 the equilibrium partial pressures of CO, Pco, as a function of C-content in the metal and process temperature is illustrated. The CO pressure can be controlled by dilution of the oxygen with inert gas. When Pco,eq>1 CO(g) can form without dilution of the gas phase with inert gas (eq. 2). From figure 1 it is seen that to decarburize the FeMn-metal to around 1.5%C a process temperature of 1700^{o}C is necessary at Pco 1 atm. To decarburize the metal to lower carbon contents a further temperature increase or a lowered Pco is necessary. However, as the vapour pressure of Mn increase when the temperature increases it is important to control the process temperature to avoid excessive Mn losses.

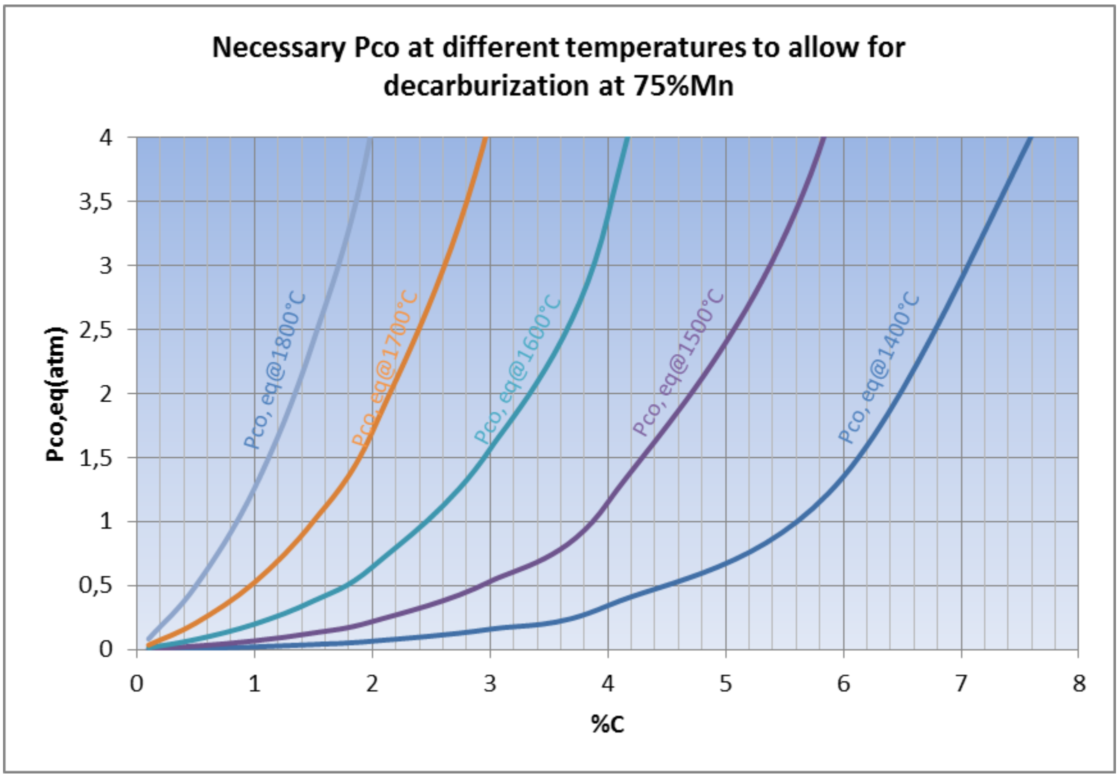

Figure 2: Required Pco as a function of temperature and %C in FeMn (75% Mn)

By diluting the partial pressure of CO, in the same manner as for stainless steel refining, decarburization is performed at more reasonable temperatures and lower final carbon contents can be achieved. The steam in the CLU process is a unique tool in this respect. Hydrogen from the decomposed steam dilutes the CO to lower its partial pressure and is thereby favouring the decarburization, as described in paragraph 3.1.This has also been discussed by the authors in previous papers [7].

During the process oxygen, steam and argon gas is mixed to optimize the process conditions. As the solubility of nitrogen is high in manganese, nitrogen gas is not an alternative unless nitrided products are being made.

3.3 Fundamentals of FeCr refining

The fundamentals of FeCr refining can be described similarly as for FeMn refining, and is only described shortly in this section. The important reactions that describe the decarburisation process are:

$C + ½ O_2 (g) = CO (g)$ (6)

$2 \underline{Cr} + 3/2 O_2 (g) = Cr_2O_3$ (7)

Where the sum reaction can be expressed as

$3 \underline{C} + Cr_2O_3 = 2 \underline{Cr} + 3 CO (g)$ (8)

$$K_8 = \left(\frac{a_{Cr}^2 \; x P_{CO}^3}{a_{Cr2O3} \; x \; a_C^3} \right)$$

K_8 is the equilibrium constant for reaction (8).

Similarly as for FeMn refining the carbon removal is favoured by a high temperature, a high activity of C and Cr_2O_3, a low activity of Cr and a low partial pressure of CO.

During the refining elements with high affinity for oxygen will be removed first such as Si, Ti and Al. These are all strong exothermic reactions generating heat in the process. Once the temperature has increased sufficiently the de-carburisation becomes the dominant reaction. Initially the oxygen supply limits the decarburisation rate.

As the decarburisation process progress inert gas in the form of steam is supplied to lower the partial pressure of CO to promote the decarburisation further and to balance the excess heat in the converter. Similarly to the Mn-refining, alternative gases as Ar and N_2 may be combined with the steam to reach certain objectives.

During the decarburisation the temperature must at all times be controlled to ensure that it is neither too low to promote oxidation of chromium or too high to prevent excessive lining wear.

4 CLU CONVERTER PLANT

In the CLU converter process there are several important tasks during the refining operation of FeCr and FeMn that has to be considered, and the most important are summarized below.

- Refine HC ferroalloys into correct analysis, mass, process time and tap-temperature
- Economic use of raw materials, gases, additives, etc.
- Maximize the yield of Cr and Mn-units
- Minimize cost of refractory
- Have the flexibility to produce different grades and handle sudden shortages
- Produce a minimum of slag with the right quality
- Ensure a safe and repeatable processes with high availability
- To be energy-efficient with minimal environmental impact

From this design perspective UHT has focused on providing a state-of-the-art solution for process control as to both predict and simulate the outcome of the refining and to control the output result in real-time.

To ensure that the defined optimal process is executed, there is a need for highly accurate and reliable gas mix-ing station and raw material handling system as well as a converter vessel which has the appropriate design as well as reliable and trouble-free support systems as the hydraulic drive, water cooled top lance, stainless steel tuyeres and a efficient evacuation systems for off gases.

In table 2 some CLU and GRANSHOT references for ferroalloys are presented.

Table 3: CLU & GRANSHOT references for FeMn&FeCr

Customer	*CLU converter*	*Material*	*Country*	*Comment*
-	*25 ton*	*MC FeMn*	-	-
-	*12 ton*	*MC FeMn*	-	-
AFARAK Mogale Alloys	*13 ton*	*MC FeCr*	*South Africa*	*With GRANSHOT*
FerroChrome Furnaces	*4 x 8 ton*	*MC FeCr*	*South Africa*	*With GRANSHOT*
Mengfa Alloys	*25 ton*	*MC FeMn*	*China*	-
ThosBegbie	*10 ton*	*LC FeCr*	*South Africa*	*With GRANSHOT*
MEL	*25 ton*	*MC FeMn*	*India*	-
SamancorFerrometals	*25 ton*	*MC FeCr*	*South Africa*	*With GRANSHOT*

4.1 Real-time Process Control

UTCAS is a real-time process control system specially designed for converter refining. The system includes an effective process control as well as tools for process design and production evaluation; see Figure 3. This system is used both in stainless steelmaking and ferroalloy production.

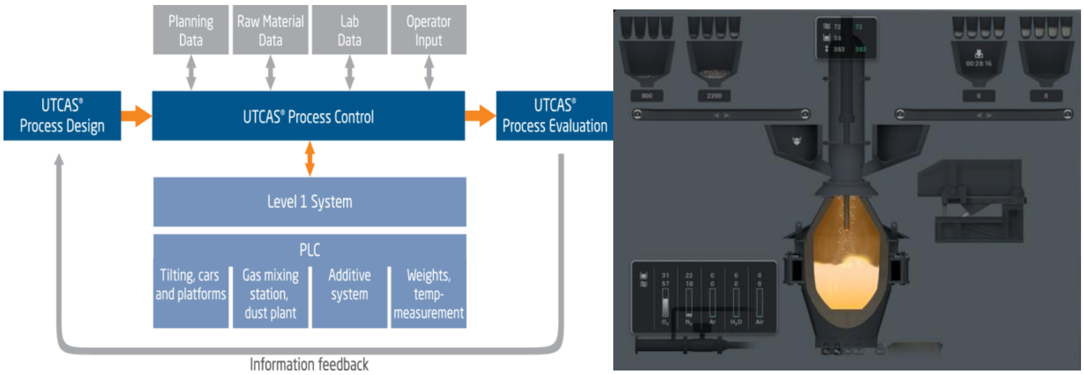

Figure 3: All aspects of ferroalloy refining are handled by the UTCAS Process Control system.

The UTCAS system includes a set of validated metallurgical models capable of determining heat and mass balance and chemical composition continuously during the process. The models are also used to generate a forecast, a prediction, of the final temperature and slag/metal composition based on planned gas blowing and additions.

The prediction is used as a valuable tool when designing the process prior to production and also during processing by optimizing and controlling the process in order to meet the final targets.

4.2 Rugged Converter Design

The main aspects of designing a converter is to make sure that it is reliable with a minimum of maintenance and that its operations are fully controllable and repeatable. The typical size of a CLU converter for ferroalloys is 5-40 tonnes. This size is defined by tapping volumes that is available from the up-stream reduction furnaces.

The CLU process is operated in a vessel lined with basic refractory such as dolomite or chrome magnesite. Process gases are introduced through submerged tuyeres that are installed through the refractory. A water-cooled top-lance is used in converters with bigger nominal size than 15 t during the initial phase of the process to cut the processing time.

Figure 4: The CLU converter vessel in a trunnion ring fitted with a hydraulic motor (right).

The converter vessel is fixed in a trunnion ring that allows the converter to rotate by a hydraulic motor for different positioning during metal and material feeding, blowing, sampling and tapping, see Figure4. The gas mixing station distributes the defined process gases as required by the UTCAS process control system. UTCAS also provides all the data necessary to control the material handling system.

From the control room the process operator runs the refining process using the UTCAS system, Figure 5. In front of the converter the operators inspect the converter and take samples of metal composition and temperature. Additions of alloys, fluxes and scrap are fed during the refining process from the automated material handling system but also by the use of crane or hydraulically operated skips. The refining process generates carbon monoxide which is collected and combusted in the water-cooled hood installed over the vessel. These flue-gases are further handled in the downstream fume treatment plant, FTP.

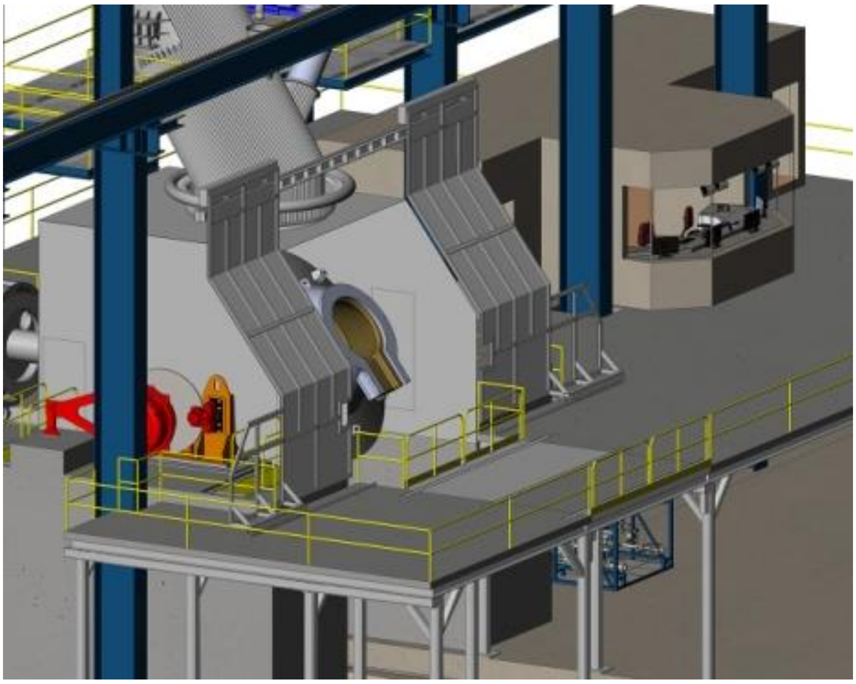

Figure 5: The process control room is here placed to the right of the converter vessel.

5 FeCr refining at AFARAK Mogale Alloys, South Africa [8]

On the 17th of December 2014, AFARAK announced that the Mogale Alloys plant has completed the installation of a CLU ferroalloy refining and GRANSHOT metal granulation plant, Figure 6. Significant part of the current ferrochrome production can now be converted to granulated medium carbon ferrochrome. This affects positively the profitability of Mogale Alloys and moves the AFARAK group further into mature markets and several long term sales contracts of the new specialty alloy material has already been secured.

The total cost of the investment was approximately 12.9 M€ and the monthly production capacity of the plant is expected to be 1,500 tonnes of medium-carbon ferrochrome, MC FeCr.

Figure 6: CLU refined FeCr granulated at AFARAK Mogale Alloys plant in SA [8].

5 CONCLUSIONS

The use of refined FeMn increases faster than the rest of the FeMn market, this implies that more refining capacity is desired. The CLU is the most versatile process to meet this capacity demand.

There is potential to develop the FeCr market with new niche products that is best produced with the CLU process.

The CLU process gives unique cost benefits and high yield in both FeMn- and FeCr-refining.

Afarak has recently proven that installation of a complete CLU converter refining and GRANSHOT granulation project with all necessary buildings and other infrastructure can be made in a short time and with limited capital expenses.

With the real-time process control system UTCAS, all aspects of modern ferroalloy refining are handled enabling excellent process control that optimizes the process for every situation.

6 REFERENCES

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