INNOVATIONS IN FERROALLOYS PROCESS TECHNOLOGIES

Thomas Germershausen, Jan Bader, Jan Reichel, Uwe Gerike;

SMS Siemag AG, Eduard-Schloemann-Strasse 4, Düsseldorf, Germany;
e-mail: jan.bader@sms-siemag.com

ABSTRACT

SMS Siemag is part of the SMS group. With its predecessor companies the company serves the needs of the global metals industries for more than 250 years. The SMS group has grown over the centuries and has got among others the following companies as its ancestors namely Mannesmann Demag, MAN GHH; Krupp Industrietechnik. With 10,000 employees worldwide working for the group the annual order intake is in the range of 3.5 billion €. About 60 % of the personnel are based in Germany.

The SMS group supplies the complete range of technology for metals production and processing, starting with pelletising and pig iron production through the complete chain of metals processing and ferroalloy production including finishing lines and processing technologies for non-ferrous metals.

For the ferrous- and non-ferrous industries SMS Siemag provides technologies like reduction furnaces, electric smelters (SAF), and refiners. Steelmaking plants for the production of carbon and stainless steel are supplied with EAFs, S/EAFs and CONARC® plants as well as BOFs, AODs, Kaldo (TBRC) and special converters including vacuum treatment plants.

Recent extended offer of SMS Siemag AG concerns such technologies as

- *FeNi converters*
- *Kaldo converter, e.g. in Lünen for Cu production*
- *FeMn converter, e.g. in Bushan*
- *FeCr refining in a vacuum converter with CO_2 injection.*
- *EAF for FeMn production from recycled batteries*
- *FeNi refining in ladle stands, e.g. at Koniambo*

A special position takes the SMS group in the environmental technologies. It supplies gas cleaning and energy recovery plants. Additional and special services like material handling, electrical and automation systems, turnkey solutions, maintenance strategies and financing are also a part of the SMS Siemag portfolio.

1. FERRO MANGANESE REFINING IN AOD PROCESS. BHUSHAN PLANT / INDIA

More than 90% of the manganese ore mined is used in the steel industry. The most usual way in which manganese is added to steel is as ferromanganese, silicomanganese or electrolytic manganese. Ferromanganese alloys may be general divided into three groups:

- FeMnHC high carbon ferromanganese, with approx. 70% manganese, max. 7.5% carbon and 0.4-0.6% silicon,
- FeMnMC medium carbon ferromanganese , with > 75% manganese, 1.0-1.5% carbon and < 0.8% silicon,
- FeMnLC low carbon ferromanganese, with approx. 80-83% manganese, < 0.5% carbon and 0.6% silicon.

After the carbothermic reduction in Submerged Arc Furnace (SAF) FeMnHC contains still high amount of carbon. The metal with a temperature of about 1350°C is tapped into ladles and transferred to the AOD converter. Further decarburization of FeMnHC has the goal of decreasing carbon content to a level corresponding to the metallurgical and commercial requirements. High initial content of carbon and its high affinity to oxygen makes the process strongly exothermic. In consequence, the metal is strongly heated and requires highly efficient cooling. The temperature of the manganese refining process has to be 1700-1750°C. Higher temperature levels lead to several problems, such as severe refractory attack, difficult casting of superheated metal, and difficult slag/metal separation. Another issue encountered is the very high vapour pressure of manganese leading to excessive evaporation and oxidation by excess oxygen. Oxidized manganese is collected mainly as Mn_3O_4 in the gas cleaning system. The oxide dust can be agglomerated and recycled in the FeMn furnace (SAF) for recovery of Mn. The economy of the process is highly dependent of the recovery of manganese in the refined alloy. The total yield of manganese with this process technology is 92% and above.

All the features are considered in the concept of the Bhushan´s order to SMS Siemag AG granted in October 2010. Figure 1 shows the concept of the plant in Orissa/India.

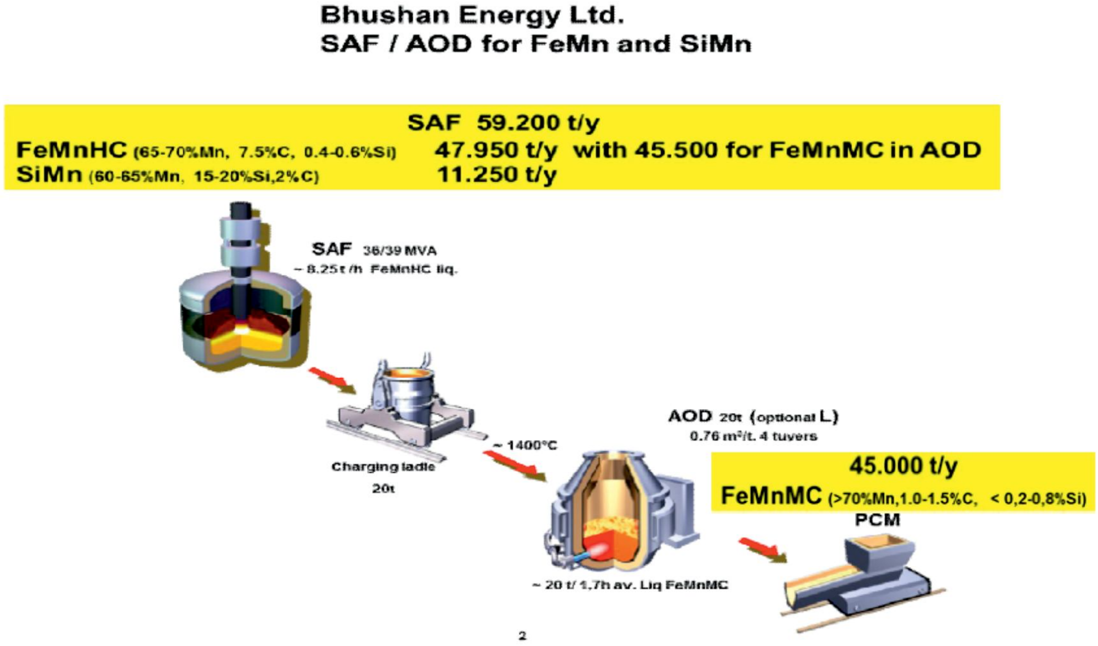

Figure 1: Concept of FeMn - Plant Bhushan/India

2. FERRONICKEL REFINING

By far the most amount of FeNi alloys are used as alloying elements in the stainless steel industry. Particularly for the FeNi that is used in the secondary metallurgic process steps in the stainless steel melt shops alloys with low concentrations of impurities are demanded. Process technology as well as plant equipment that is required for the refining treatment is strongly dependent on the quality of the FeNi that is tapped at the smelter and the desired quality of the final FeNi alloy product. Most frequently the raw FeNi from the smelter is polluted with some sulfur which makes it necessary to perform a subsequent desulfurization step. But there are also other elements that may occur in higher concentrations, also in combination with sulfur, i.e. silicon, carbon and also chromium or phosphorus that can be in the focus of a refining process. Most decisive for the choice of refining equipment are the concentrations of carbon and silicon in the liquid raw FeNi. Generally saying, in the case of carbon and silicon concentrations not much higher than 0,6 %, respectively, usually all of the required metallurgical treatment steps can be performed in line with a ladle treatment process. Such a ladle treatment refinery has already been designed by SMS within the scope of the Koniambo project. A target analysis for such a ladle refining process is exemplarily given in this table:

Composition (wt%)			
C	**SI**	**P**	**S**
$\leqslant$ 0.03	$\leqslant$ 0.20	$\leqslant$ 0.03	$\leqslant$ 0.03

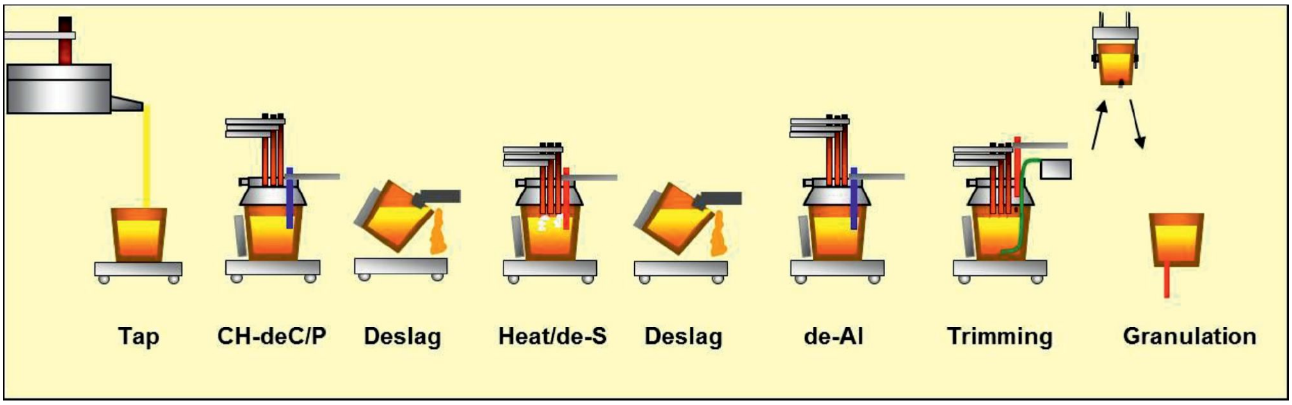

Figure 2: Example for a ladle refining process for removal of phosphorus, carbon and sulfur

Figure 2 shows a schematic example for the sequence of a ladle refining process for removal of phosphorus, carbon and sulfur. Usually FeNi alloys are tapped at temperatures not very far above their liquidus temperatures. That is why heating of the tapped metal is necessary after tapping before further treatment steps can be started. Heating can be performed by chemical heating, i.e. oxidation of silicon or aluminum in the liquid metal by blowing oxygen with a lance, by electrical heating in the ladle Furnace (LF). For proper mixing and homogenization in the ladle electromagnetic stirring or gas purging with help of a porous plug in the ladle bottom are recommended. Heating of the liquid metal allows subsequent additions of fluxes, e.g. lime, for the generation of a slag that is suitable for the refining treatment. Phosphorus and also carbon can be removed by further oxygen lance blowing according to eq. (1) and eq. (2):

$$2[P]+5[O]=(P_2O_5) \tag{1}$$

$$[C]+[O]=\{CO\} \tag{2}$$

By contrast to decarburization and dephosphorization reactions desulfurization generally requires a very low oxygen activity. Therefore the slag which contains oxidation products like SiO_2, FeO, P_2O_5, has to be removed by deslagging before subsequent desulfurization in the ladle furnace. Prior to desulfurization the soluble oxygen in the metal is killed by addition of aluminum. Electrical heating in the ladle furnace allows addition of fluxes with high basicity to form a liquid and reactive slag for the desulfurization process according to eq.(3):

$$3[S]+3(CaO)+2[Al]=3(CaS)+(Al_2O_3) \tag{3}$$

Intensive mixing of slag and liquid metal is required to promote the transfer of sulfur from the metal into the slag. For this purpose stirring should be supported by nitrogen injection with a refractory lance.

At the end of desulfurization the sulfur containing slag is removed in a deslagging step. Subsequently, to prepare the liquid FeNi for the final granulation process remaining aluminium is removed by a small amount of oxygen injection followed by some CaSi wire feeding (trimming step) combined with stirring for further desulfurisation.

At carbon and silicon levels significantly higher than 0,6 % a converter process will be necessary due to high generation of slag and the tendency of slopping and spatter during the oxygen blowing process when it is done in a ladle under such conditions. Due to the higher specific volume of a converter vessel, very good mixing intensity and the opportunity to control the slag analysis with a suitable material handling system high desiliconization and decarburization rates are achieved which is fundamental for high plant productivity.

3. INNOVATIONS IN FERROALLOY TECHNIQUE

3.1 Ferrochromium treatment in vacuum converter with CO_2

On base of the vacuum technique and converter technology SMS Siemag AG has developed a novel technology for ferroalloy production. The silicon-carbon refining process is performed by oxygen and carbon dioxide introduction into the melt by a top lance and bottom tuyeres. The new development is an alternative to a conventional treatment in secondary metallurgy devices.

The subject of the technology is ferroalloy production by refining principal of carbon, silicon and phosphorous if required at minimizing solid cooling materials mostly of final products like alloys medium carbon. In comparison with conventional technologies the solid material for cooling can be reduced up to 50% due to the cooling by carbon dioxide. Strong endothermic reaction of carbon dioxide with all components of the melt allows exact control of the refining process and the temperature. Dependent on the required final carbon content a reduction of carbon monoxide pressure as driving force of decarburization is controlled by external pressure. The pressure can be obtained by a vacuum system. Deep decarburization to low carbon contents can be achieved by additional inert gas blowing.

This technology is related to all alloy refining processes independent on the initial conditions of the input materials. Industrial tests confirmed all benefits of the technology and show many significant economic benefits. Shorting of the treatment time, low consumption of cooling material and high yield of the main alloy component are the significant features of the new technological solution. Further benefits are:

- reduction of thermal losses due to the complete treatment in one vessel
- smaller plant footprint
- saving investment costs
- saving operating costs as refractory, process gases, reducing agents, personnel
- less free board of casting ladle
- lowest nitrogen and hydrogen contents in the final product

3.2. Vacuum converter process. fundamentals

The subject of the technology is ferroalloy production requesting different refining grades. High initial carbon and silicon contents classify all the refining processes to the strong exothermic ones with high demand of cooling. But independent on the kind of the main element in the alloy the decarburization of the process has the same characteristic as carbon or stainless refining process. The treatment is principally divided into two steps, into the main decarburization and the dynamic step, figure 3. Both steps are separated by the so called critical carbon content. All recorded courses of decarburization processes with time confirm such decarburization characteristic.

In the main decarburization step the time span depends on the blow parameters and in the dynamic period it depends on the thermodynamic potential of the carbon oxidation.

Blowing rates of oxygen in the main period determine the level of decarburization speed, eq.(4). After the critical moment the decarburization speed is controlled by thermodynamical potential of decarburization expressed by the difference between the current and the equilibrium carbon concentration, eq.(5).

$$\left(-\frac{dC}{dt}\right)=\frac{100}{W}\frac{12}{11.2}Q_{O_2C} \tag{4}$$

where:

Q_{O_2C} - oxygen flow rate reacting with carbon

W - metal weight

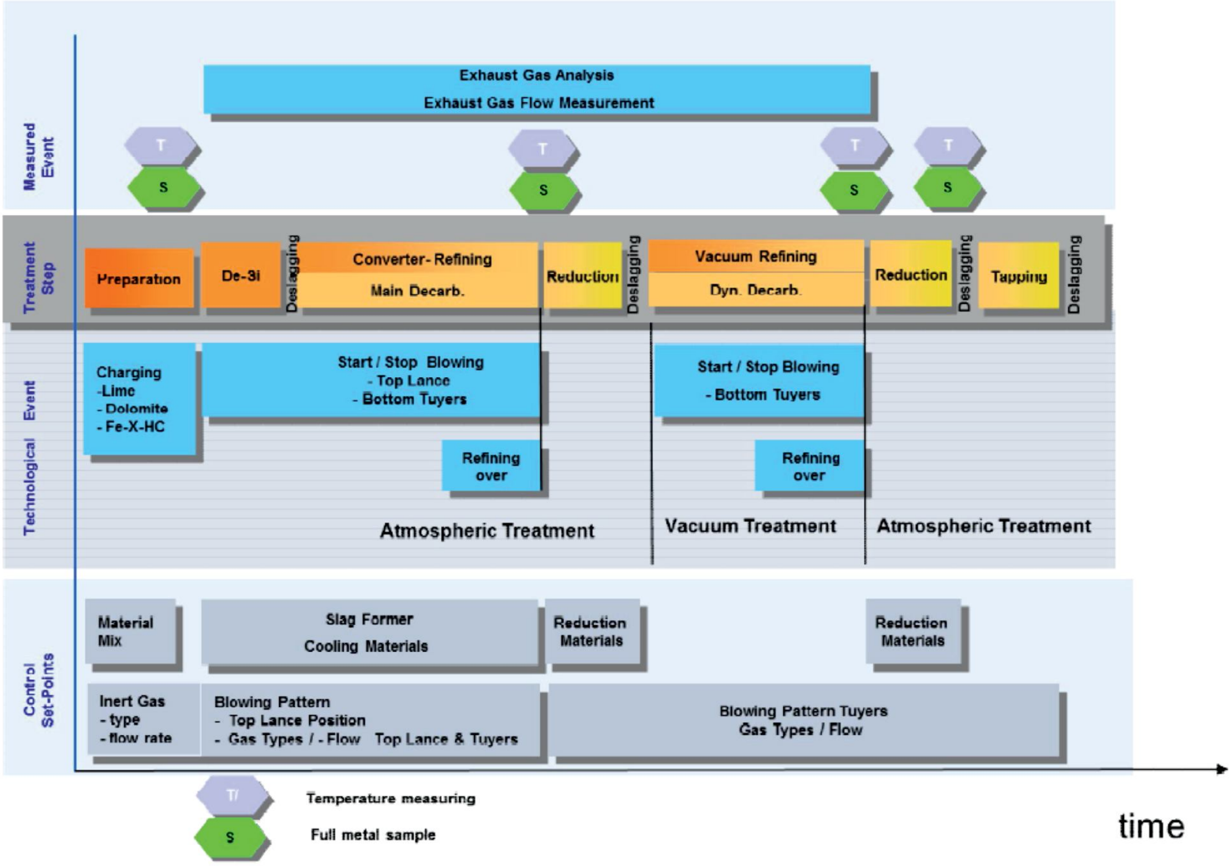

Figure 3: Vacuum Converter technology

Upon reaching the critical moment, the rate of carbon transport to the reaction places in the metal becomes limitation. The decarburization rate may be approximated by

$$\left(-\frac{dC}{dt}\right)=k_C\frac{A}{V}\left(C-C^*\right) \quad (5)$$

where:

k_C - mass transfer coefficient

A - active reaction surface

V - volume of the metal

C, C* - current and equilibrium carbon concentration in the metal respectively.

From the practical point of view it is difficult to accurately predict either kc or the interfacial active area A. However, estimates may be made regarding the order of magnitude of these quantities from turbulence theory, since both the interfacial active area and the mass transfer coefficient are related to the rate of turbulence energy dissipation. For this reason, the two quantities can be combined into a single parameter “ $\frac{1}{\tau}$ ”, the overall oxygen exchange coefficient:

$$\frac{1}{\tau}= k_C\frac{A}{V} \quad (6)$$

The dimension of τ is the second, so it is convenient to define it as a reaction time constant of the decarburization. Thus, the rate of decarburization is expressed by

$$\left(-\frac{dC}{dt}\right)=\frac{1}{\tau}\left(C-C^*\right) \quad (7)$$

Uncontrolled oxygen blowing after passing of the critical point results in high metal oxidation with extremely high rise in temperature. It is quite understandable that the control of oxygen and the carbon in equilibrium requires an adaption of the blowing pattern at that critical point.

This adaption changes the supply of oxygen to the decarburization and consequently results in a minimum oxidation of metallic components as well as it prevents indirectly an excessive temperature rise. It may be stated that the optimal process control during the dynamic step determines the economic effects of the total process. The finding of optimal conditions requires analysis of the process kinetic represented by decarburization course. It is determined by the following oxidation reactions:

$$[C]+[O=\{CO\}] \quad (8)$$

$$n[Me]+m[O]=\left(Me_nO_m\right) \quad (9)$$

$$\left(Me_nO_m\right)+m[C]=n[Me]+m\{CO\} \quad (10)$$

From eq (10) the process equilibrium can be expressed as

$$K(T) = \frac{a_{Me}^{n} p_{CO}^{m}}{a_{Me_nO_m} a_C^{m}} \tag{11}$$

and at the carbon activity as

$$a_C = f_C C^* \tag{12}$$

the carbon equilibrium is equal

$$C^* = V^*\left(Me, X, T, a_{Me_nO_m}\right) p_{CO} \tag{13}$$

where
Me - main component of the melt
V* - complex function dependent on metal chemistry, temperature, slag oxide activity
X - co-existing elements as Si, P, S etc.
T - melt temperature
$a_{Me_nO_m}$ - oxide activity of the main element
p_{CO} - carbon monoxide partial pressure

and because

$$p_{CO} = \frac{N_{CO}}{N_{CO} + N_{IG}} p \tag{14}$$

where

$$N_{CO} = k_1 \left(-\frac{dC}{dt} \right) \tag{15}$$

represents the number of removed CO-moles from the metal

and

$$N_{IG} = k_2 \, Q_{IG} \tag{16}$$

represents the mol-number of inert gas at an operating flow rate Q_{IG}, the main principle of the decarburization control by vacuum converter can be expressed as

$$\left(-\frac{dC}{dt} \right) = \frac{k_1 \left(-\frac{dC}{dt} \right)}{k_1 \left(-\frac{dC}{dt} \right) + k_2 Q_{IG}} p \tag{17}$$

It can be seen from the eq.(17) that there are two parameters to force the decarburization speed after the critical carbon content e.g. the outside pressure p and the inert gas flow rate Q_{IG}. In extreme case, if the outside pressure equals to the atmospheric the only possibility to control the decarburization is the inert gas flow rate (typical AOD process). In other case if inert gas flow rate is reduced to the stirring rate the control can be carried out by vacuum pressure respectively. In combination of both the control can lead to the extreme low carbon equilibriums and allows obtaining of low carbon contents. Beside of this effect in cases of standard decarburization the inert gas consumption can be significantly reduced and vacuum pressure can be increased. The control takes a two dimensional form at a constant temperature providing an optimal solution at maximal decarburization speed. Using as inert gas carbon dioxide the control of the decarburization is reduced to the outside pressure only. Figure 4 presents carbon equilibrium of a ferrochromium treatment dependent on the outside pressure and temperature. At the CO_2-blowing and at 1700°C the carbon equilibrium establishes by 1% if operated vacuum obtains a level of 200 mbar.

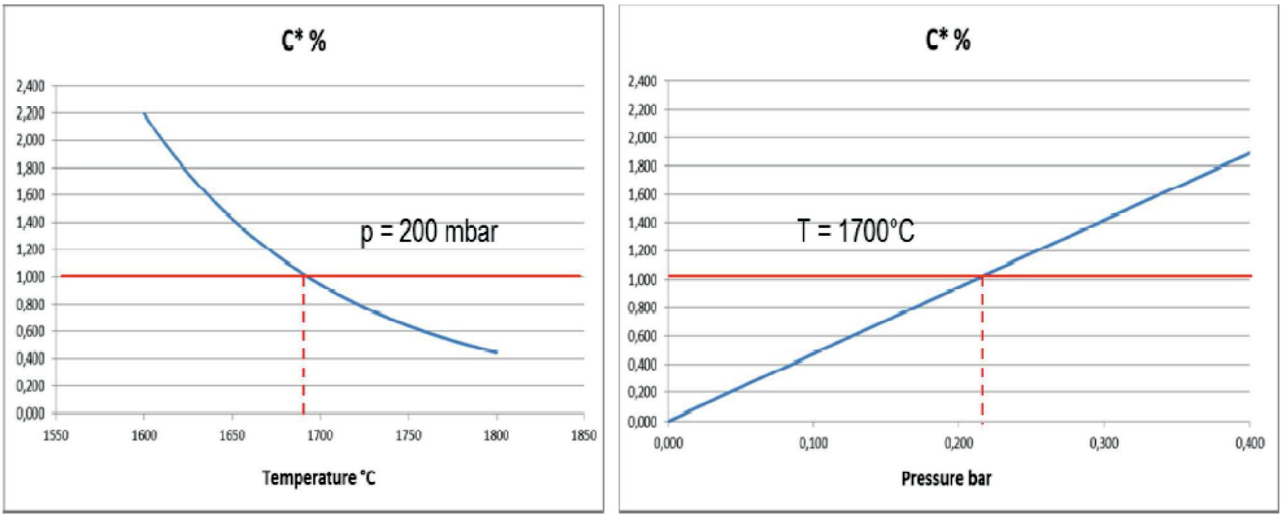

Figure 4: Carbon equilibrium of a FeCrMC alloy

Corresponding to the Boudouard –reaction the operation of CO_2 enables additional decarburization and desiliconization of the melt described as below

$$\{CO_2\}=[O]+\{CO\} \tag{18}$$

$$+$$

$$[C]=\{CO\} \;=\; 2\{CO\} \tag{19}$$

or

$$\{CO_2\}=[O]+\{CO\} \tag{20}$$

$$+$$

$$\frac{1}{2}[Si]=\frac{1}{2}(SiO_2) \tag{21}$$

Both reactions are strongly endothermic and support the main oxidation reactions with additional oxygen coming from CO_2 dissociation.

3.3. The vacuum converter pprocess and equipment

Technical realization of the vacuum converter with features described before leads to a converter construction with bottom blowing and movable cover. Due to the different oxygen blowing rates operated during the main and dynamic decarburization steps a dedusting system requires two separate constructions as well. In the vacuum converter the active reaction area is larger in comparison with conventional processes especially in case of CO_2-operation. Optimal geometry of the converter expressed in ratio bath diameter - bath height as well high specific converter volume favor intensive mechanical metal mixing by inert gas and high CO-development. The process is operated in the main step by combined blowing top lance and bottom tuyers only. It accelerates the decarburization and shorts the treatment time. The oxygen blowing during the vacuum step is reduced to the bottom blowing. Operation with CO_2 increases the oxidizing potential and is carried out by bottom tuyers as well.

Both steps the main and dynamic are finished by a slag reduction on the conventional way. Samples and temperature measurements at the process start, after the desiliconization, the main and the dynamic step as well as at the tapping complete the operations during the treatment.

Figure 5 demonstrates the general construction of the vacuum converter. The connection between the converter vessel and the movable cover is established by an insulated water cooled flange below the converter mouth.

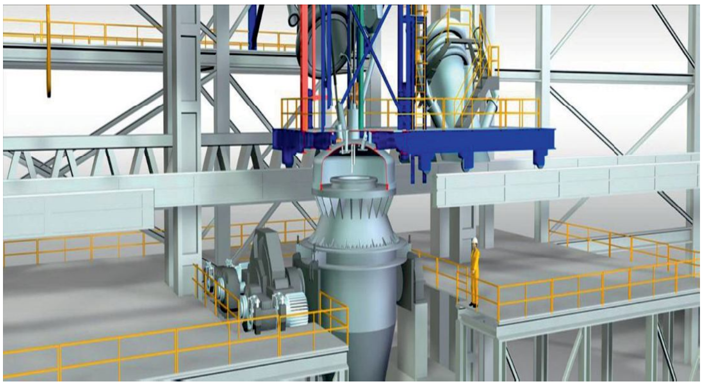

Figure 5: Vacuum converter in vacuum step operation

Via steam injector and water pump system a vacuum pressure can be controlled in the complete range between 1 and 1000 mbar whereby the lowest vacuum defines the target final carbon content.

The process gas supply - oxygen, carbon dioxide, argon and nitrogen is connected to the bottom tuyers via trunnion ring. The number of tuyers varies dependent on the converter size. Typical middle size converter in the capacity range 20-25t disposes with three bottom tuyers. The temperature control is ensured by a continuous material addition system with a charging rate corresponding contrary to the increasing temperature gradient of the process.

3.4. Vacuum converter with CO_2-industrial test

On the basis of laboratory test results made at the AGH University of Science and Technology / Cracow Poland SMS Siemag AG agreed industrial tests of ferrochrome high carbon refining on a modified 10t vacuum converter by Metso Minerals Oy in order to prove the novel refining technology and its industrial functionality and viability. The tests were carried out in the foundry in Tampere, Finland, figure 6.

The original VOD converter and the EAF both with a capacity of 15t designed for production of austenitic and ferritic steel grades have been modified by SMS Siemag, figure 7.

The EAF dolomite refractory was exchanged to chromite-magnesite due to the high melting temperature of the FeCrHC resulting from the high liquidus temperature. High temperature losses at the melt transfer and charging into the converter intensify the necessity of higher EAF tapping temperature. The average EAF tapping temperature was approx. 1800°C +/-10°C and the initial treatment temperature at the converter was 1710°C. Figure 8 shows measured liquidus trend of the FeCrHC with 7,3%C and of the FeCrMC with 1% C: It can be recognized a liquidus temperature of the FeCrHC at 1670-1680°C and of the FeCrMC with 1% at 1260-1264°C.

The original blowing system consisted of a top lance only has been extended to the two additional bottom tuyers, through which oxygen, argon and CO_2 were blown. The gas control was realized by a valve station and computer control system developed especially for that configuration. Due to the restricted capacity of the dedusting system the oxygen blowing rates inclusive CO_2 were limited to 10 Nm^3/min.

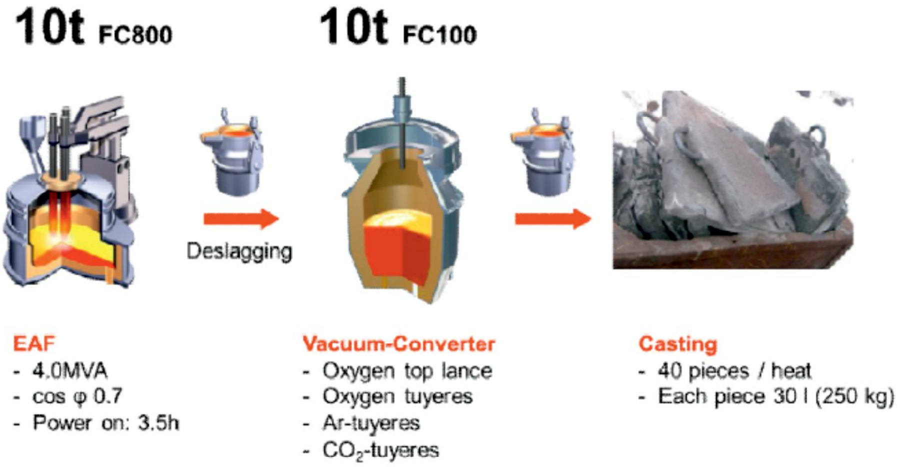

Figure 6: FeCrHC refining process line by vacuum converter

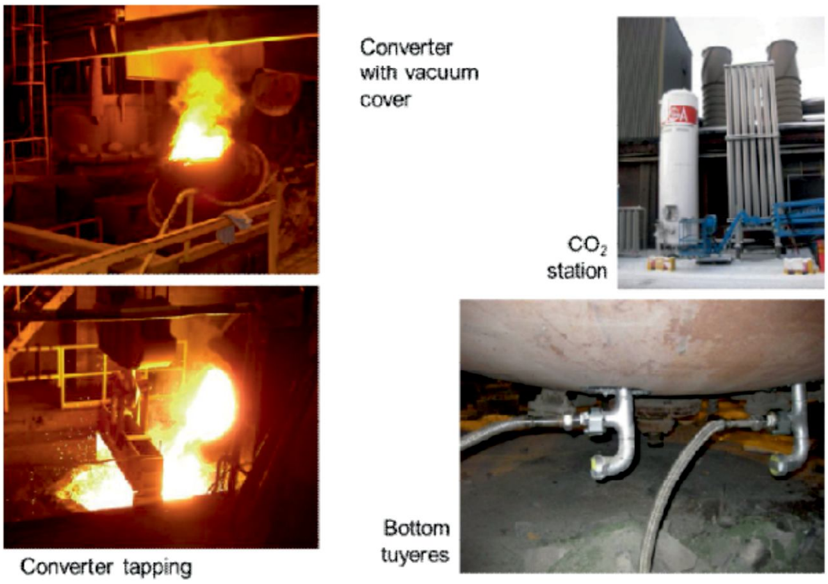

Figure 7: Some impressions of the test installations at the Metso Minerals Oy facilities

Besides of modified parts of the refractory and blowing system also the original vacuum system required changes. The original system works usually always under vacuum. Immediately after process start the vacuum decreases to the level of 200 mbar. However, the new treatment design of the main decarburization foresees an atmospheric pressure. That was ensured after an integration of a vacuum leakage air flap. Finally the pressure during the main decarburization was controlled on the level between 700 and 800 mbar. The final vacuum step after the critical moment was operated on the level of 200 mbar. The metallurgical test results confirmed the theoretical process calculations.

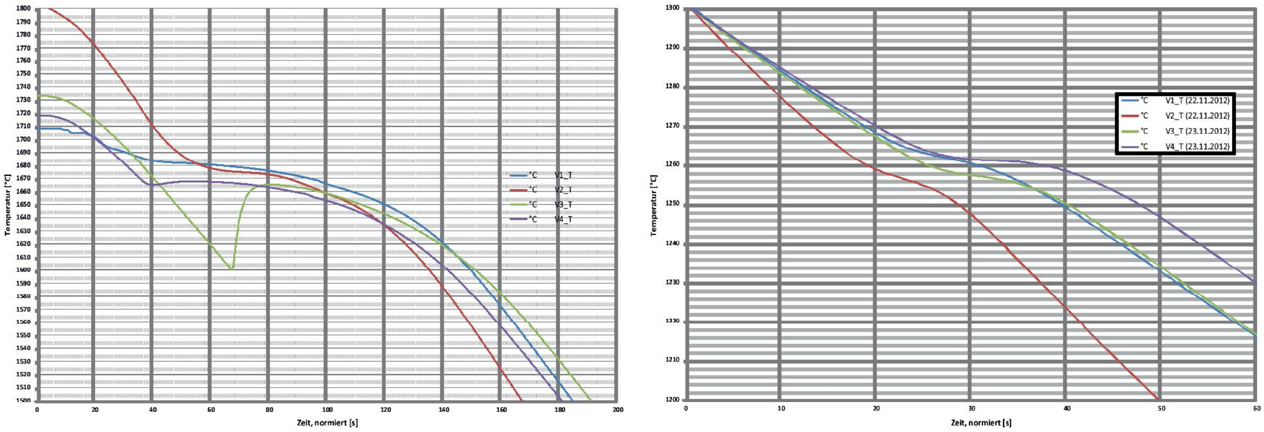

Figure 8: Measured liquidus temperatures of tested input and output FeCr

From the metallurgical point of view it can be said that the technology has limits in its decarburization dependent on the vacuum level used during the dynamic step and the temperature. Figure 3 shows the limits as 1700°C and 200 mbar. However, to reach surely lower carbon contents the lower level of vacuum at a moderate temperature around 1700°C is inalienable. It was shown that the FeCrHC with the initial chemistry

	C%	Si%	Cr%	P%	S%
	8.5	0.95	70.8	0.03	0.04
was transformed into FeCrMC with:	1.0	0.30	72.9	0.03	0.04.

and with a chromium yield of 95.6%.

Table 2 shows the process schedule in treatment steps. As can be seen the main decarburization was divided into six steps caused by divided batch additions of slag former and cooling materials. The deep vacuum step started at the critical carbon content at around 1.9%. The measured and calculated values of the critical carbon concentration showed high conformance.

Table 2: Process schedule in treatment steps

Table 2	**VC – Operation**				
Operation		**C, %**	**Si, %**	**Cr, %**	**T°C**
1	Start	8.5	1	70.8	1700
2	DSi	8.5	0.05	70.8	1700
3	1MDC	6.9	0.05	70.8	1702
4	2MDC	6.05	0.050	70.5	1713
5	3MDC	5.27	0.050	68.8	1713
6	4MDC	4.5	0.050	69.6	1691
7	5MDC	3.72	0.015	69.6	1716
8	6MDC	2.95	0.071	71.4	1703
9	Reduction				
10	1DDC (Vacuum	1.91	0.015	71.9	1691
11	2DDC (Vacuum)	1.46	0.015	70.6	1731
12	Reduction	1.00	0.400	70.6	
13	Tapping	1	0.400	73.7	1663

4. SUMMARY

Innovative process routes for the refining of FeMn, FeNi and FeCr have already been built by SMS.

Advanced FeMnHC refining technology on the basis of AOD converter has been developed and presented in this paper.

This FeMnHC refining process achieves yields of 92% and above.

Refining of FeNi in BOF converter as well as in ladle treatment station has been built. Selection of most suitable process route depends on liquid raw FeNi analysis and desired product quality.

The industrial test of FeCrHC refining carried out in the vacuum converter confirmed the feasibility of the new technology.

Final carbon content is strongly dependent on the melt temperature and vacuum. Both determine the carbon equilibrium at the final state.

The refining process is characterised by high potential of chemical energy due to the high initial carbon and silicon content.

Application of carbon dioxide to the process decreases significant solid cooling material requirements, as well as reduction of the treatment time.