

Strategies for Use of Superheated Steam During Stainless Steel Refining in Converters

Carl-Johan Rick
Uvån Hagfors Teknologi AB
Djursholmsvägen 30
183 52 Täby, Sweden
Tel: +4630358950
E-mail: carljohan.rick@uht.se

Key words: Steam, stainless steel, refining, converter, argon, AOD, CLU, process control

INTRODUCTION

Superheated steam has been used as a process gas in stainless steel production since the early 1970's when engineers at Uddeholms Degerfors Steel-plant developed the technology ¹. In France a similar development took place within the Creusot-Loire group. The developed process was named CLU from Creusot Loire Uddeholm-process.

Between 1973 and 2003 stainless steel was refined in Degerfors in an 80-ton converter where superheated steam, argon, nitrogen, oxygen and compressed air were used as process gases. Over the years the technology had a moderate expansion and in total seven plants has used superheated steam as a process gas industrially until now.



Figure 1. Heat exchangers and insulated pipes in steam/AOD-gas mixing station.



Figure 2. Columbus twin 120 t converters are operating with steam as a process gas.

The initial incentive to develop the technology was the desire to use the main benefit of the AOD-process, i.e. to lower the partial pressure of carbon monoxide by assistance of inert gas purging ^{2,3}. The reason why a new technology was developed was mainly to reduce the need for large quantities of at the time rare and expensive argon.

Still there are geographical locations where argon is in short supply. In 2007 argon demand greatly exceeded the supply on the South-African market and due to this fact Columbus Stainless took action to enable steam-blowing in their process⁴.

Columbus Stainless is along with North American Stainless non-Spanish members of the Acerinox group. Between 1995 and 2002 Columbus used steam in their refining process. However in 2002 a decision was made to remove the steam blowing capacity as the market then provided enough argon to satisfy the local demand and at the same time some of the original boiler equipment was worn out.

In 2008 steam-blowing capacity was reintroduced and it is now possible for Columbus to operate two converters with steam simultaneously, see figures 1 and 2.

According to Columbus production management the main motivation to reinstall steam blowing capacity with Columbus Stainless was to decrease argon peaks and to reduce the overall argon consumption to better match the local supply⁴.

This paper will not focus on Columbus operation but rather on the potential of the CLU process in general terms and on the capability of the process models verified on the Columbus site to control both the AOD and CLU processes.

BACKGROUND

Energy Management In Stainless Steelmaking

Stainless steel refining has some basic features such as carbon removal, deoxidation and desulphurisation. In the AOD process, these operations are generally combined with some alloying with solid material as well as nitrogen control by means of gas injection. From an operational point of view, the stainless steel refining is very much a matter of controlling the amount of energy available in the converter and how that energy is used, see figure 3.

The energy management situation is very different between producers due to varying local conditions:

- In converters that produce materials for stainless steel castings, the material range is wide, heat size is small and the treatment time is comparatively long. Thus the energy is almost always in deficit in these cases.
- In converters where special grades are frequent, the energy is similarly to foundry situation mostly in deficit. The deficit has the same reasons as in the foundries but the problem is smaller. During decarburisation a small heat surplus may occur during part of the time. At the end of the process a small but regular heat surplus is also common. Heat surplus also occur when the temperature is higher than expected. Instability in the production is more common for special steel-makers than for bulk-oriented producers.
- In converters that produce bulk-grade coils in the US, Japan or Europe, the scrap usually makes up a large portion of the total material input. In this case the energy is also in deficit during some part of the process. The exceptions to the heat deficit situation are similar for these converters as for the special steel producers but they occur to a lesser extent and with a lower frequency.
- In a Chinese, Indian, Latin-American or South-African situation the scrap percentage of the total metal input is usually lower than in a European plant. As a consequence, the energy is often in surplus throughout the production cycle.

When a situation with energy deficit arises in the converter it is easily handled by allowing excessive chromium-oxidation, chrome that is later recovered with silicon or aluminium. Energy deficit in the converter is avoided by melting enough material in the Electric Arc Furnace where the energy is cheaper.

The energy surplus situations are however more common. Essentially there are three practical strategies to deal with energy surplus:

- To remove the surplus by purging inert gases through the metal and heating it;
- To dilute the surplus energy by melting material to make more steel;
- To neutralize the surplus by using steam.

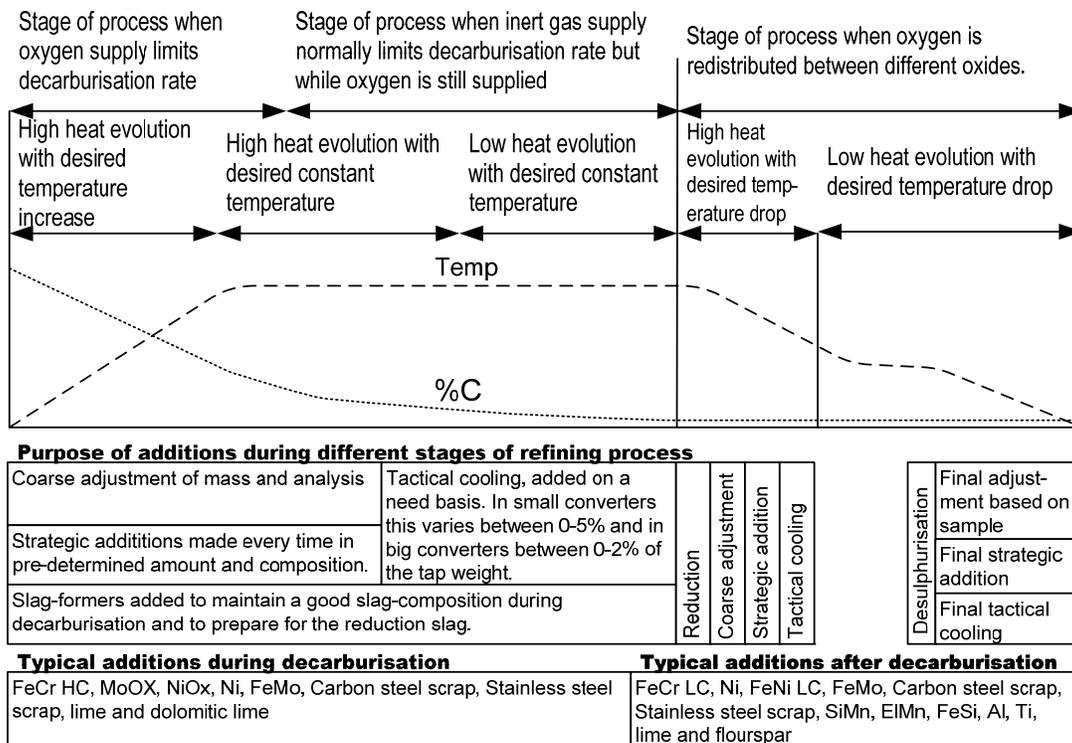


Figure 3. Typical cold material distribution and purpose during refining in AOD-converters is displayed together with brief comments on the process ⁵.

Strategies For Steam As A Process Gas

Each of the described methods above for dealing with energy surplus has its merits and applications. The most frequently used approach today is probably addition of more material to dilute the surplus energy. This paper however concentrates on the strategy to instead neutralize the energy surplus by use of energy consuming reactions, and in specific the use of steam.

Other aspects of using steam in the converter such as nitrogen-control, hydrogen, steam-production, steam-quality and the economic impact of the steam is also discussed.

The fundamental background to steam usage in the converter lies in the reduction of steam, see equation 1⁶.



The use of 1 kg of steam will substitute 1.25 nm³/Ar (or N₂), 0.625 nm³ O₂ in terms of process gas and 10 kg of scrap in terms of cooling capacity. Compared to figure 3, the steam is mainly used to substitute tactical coolants in cases where the applied strategy means that the converter operates close to its maximum capacity. Steam can also be used for cooling in cases where suitable coolants are not available or cannot be handled logistically.

Nitrogen Control In Stainless Steelmaking

Nitrogen is an important alloying element in stainless steel and it dissolves according to Siewert's law, see eq. 2.

$$[\%N]_{Equilibrium} = [\%N]_{Solubility} \cdot \sqrt{P_{N_2}} \quad \text{eq. 2}$$

Where

$$[\%N]_{Solubility} = 10^{[-188/T - 1,25 - 4373 \cdot \log[f_N]]} \quad \text{eq. 3}$$

The nitrogen solubility is defined in eq. 3 according to Chipman and Corrigan ⁷. This expression is mainly a function of the steels chemistry and temperature. For common stainless steels the solubility varies greatly, some examples are given using eq. 3 in table I.

Table I. Theoretical nitrogen solubility for some different grades and situations.

Grade	T° C	%C	%Si	%Mn	%Cr	%Ni	%Mo	N _{solubility}	Comment
ASTM 201	1580	0,04	0,3	2	17	5	0	0,29	Before Mn alloying
ASTM 201	1580	0,04	0,3	7	17	5	0	0,37	After Mn alloying
ASTM 304 L	1580	0,02	0,3	1,2	18,2	8,5	0	0,31	
ASTM 904 L	1580	0,01	0,3	1,2	20	25	4,5	0,38	
ASTM 316 Ti	1580	0,02	0,3	1,2	17	11	2	0,28	
ASTM 409	1650	1,5	0	0,5	11	0	0	0,09	After initial Si-removal
ASTM 409	1650	0,01	0,3	0,5	12	0	0	0,15	Final product
ASTM 439	1720	0,02	0,3	0,5	18	0	0	0,24	
2205	1720	0,02	0,3	1,2	22	5,5	3	0,36	Before cooling
2205	1580	0,02	0,3	1,2	22	5,5	3	0,47	After cooling

According to Siewert's law with the present application:

- Nitrogen blowing raises the Nitrogen equilibrium
- Argon blowing, along with hydrogen from steam and formed CO, lowers the Nitrogen equilibrium

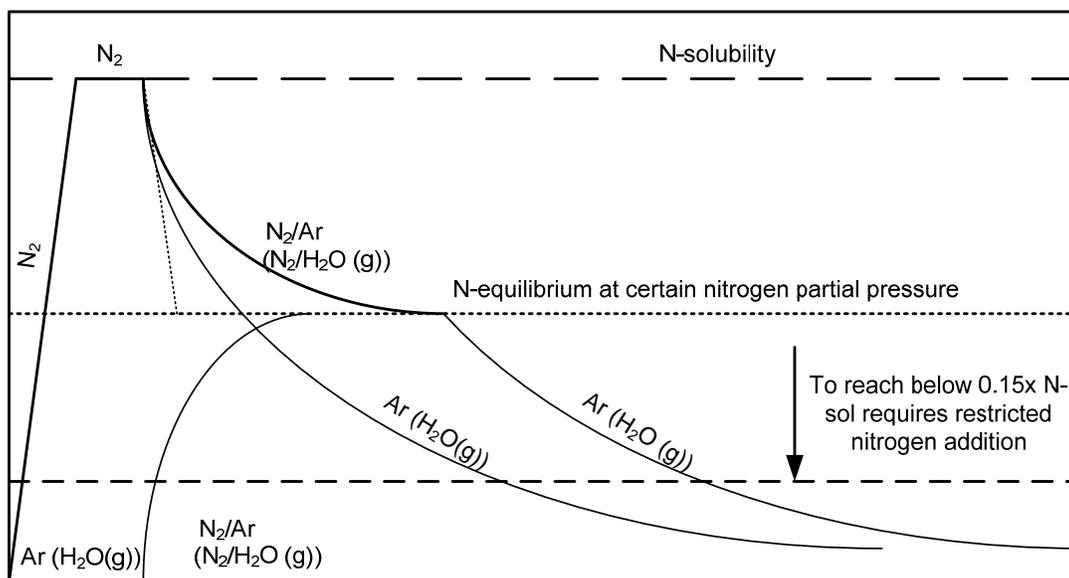


Figure 4. Principal nitrogen behavior in AOD- and CLU-process. To reach low nitrogen levels nitrogen must be avoided for a long time previous to tapping.

During different stages of the converter process the mass transfer between gas and metal and vice versa is very different. After deoxidation and desulphurisation just before tapping the mass transfer rate reaches its maximum.

For grades that have a final nitrogen target which is much lower than the solubility, see figure 4 it is often necessary to avoid nitrogen blowing throughout the process. The exception is if the heat will be treated in vacuum downstream of the converter.

For other grades it is common to initially use nitrogen and then, as late as possible, to switch over to argon.

To remove nitrogen, or to avoid nitrogen addition, steam and argon are fully substitutable until the oxygen from the steam restricts its use in the steel. This situation normally corresponds with the reduction/de-oxidation period of the process.

The benefit of steam or argon to reach low nitrogen content is twofold; the first benefit is that when these gases are used no nitrogen is added; the second benefit is that when they are added the partial pressure of nitrogen in the gas phase is lowered, which lowers the equilibrium nitrogen content and enables nitrogen removal.

Hydrogen In Stainless Steelmaking

Hydrogen from the steam dissolves in the steel in a similar fashion to nitrogen^{8,9}. Unlike nitrogen, the removal is however extremely fast down to levels below what is critical in stainless steel.

Even if hydrogen can be a problem for many types of steel, for stainless steel it is not and hydrogen levels of 5-6 ppm is normal at converter tapping for standard steel like AISI 304 independent of CLU- or AOD-processing¹⁰. Common stainless steels can be casted well up to over 10 ppm¹⁰.

Steam Production And Steam Quality

To produce steam a boiler is used. This steam must be dried using a super-heater before it becomes suitable as a steelmaking process gas. To enable blowing of dry gas in to the converter, it is necessary to preheat all process gases. This is done in a heat exchanger. A logical process flow diagram is displayed in figure 5.

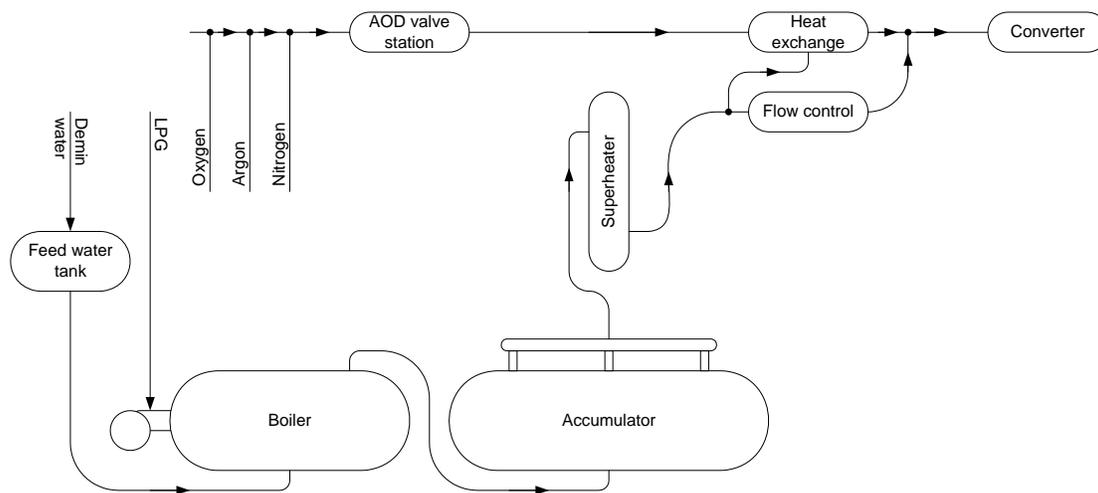


Figure 5. Typical configuration of a steam generator in relation to a refining converter

By ensuring dry gases condensation is avoided in the system and thereby risk for corrosion in pipes or moisture damage of linings is reduced.

USING STEAM

Steam Business Model

Given a situation where steam, argon, oxygen and nitrogen has known costs and where melting in the converter can be assigned a value or cost, different business scenarios can be defined. Table II compares costs for different process alternatives and situations. The cost figures should be read as relative to 1 kg of steam.

In a stainless steel plant the desire to have a good economy will normally mean that the target mass to the caster is close to the weight limit of the plant. For the AOD, which normally needs some dilution of the heat formed to keep temperature in control, cooling is necessary and the EAF will tap to leave space for the AOD to melt additional weight. In the AOD three things can happen:

- The expected heat surplus matches the weight-space delivered from the EAF in which case temperature and tap weight will be correct. (Cases 1 and 4 in table II where 10 kg of scrap is added to the AOD.)
- The expected heat surplus is less than what is required to fill the weight-space in which case additional heat has to be generated by oxidising some additional Chromium and eventually reclaiming it with additional reduction agent (FeSi, Al). (Cases 1 and 4 in table II where 10 kg of scrap is added to the AOD. In this situation an additional cost for melting can be motivated in the model, this is however not done.)
- The expected heat surplus is more than what is required to fill the weight-space in which case surplus steel has to be produced. (Cases 2 and 3 in table II where surplus metal has to be produced to manage temperature.)

For the alternative with steam available the three cases become slightly different:

- There is no need for a heat surplus instead more metal has to be melted in the EAF to make the tap weight correct. (Cases 5 and 8 in table II where 10 kg of scrap is melted in the EAF.)
- The expected heat surplus is less than what is required to use steam in which case additional heat has to be generated by oxidising some additional Chromium or steam is avoided. (Cases 5 and 8 in table II where 10 kg of scrap is melted in the EAF.)
- The expected heat surplus is more than what is required to fill the weight-space in which case steam is substituting some additional inert gas. (Cases 6 and 7 in table II where no scrap is necessary)

Because the alternative of making surplus metal is costly and creates problems it is likely that efforts are taken to keep a safe margin to avoid this situation in many AOD-operations. When steam is available this precaution is never necessary.

In the business cases presented in table II no cost has been assigned to AOD-melting compared to the cooling with steam, and no cost has been assigned to surplus melting.

The AOD-melting compared to the EAF requires better quality materials but will normally give a higher yield so a zero cost is realistic. Surplus production will however mean extra costs, often also in an environmental perspective.

Based on table II, it is evident that the benefits of using steam are dependent on the process situation. To be able to deal with this in production it is necessary to have an understandable model to base decisions on. The model in figure 6 illustrates steams usefulness from an economical perspective. The environmental impact is directly related to the economy as all costs are caused by energy purchase on the same market.

An example of steam usefulness using figure 6 follows; during the time of processing of standard 304 it is likely that steam usefulness starts in the lower left corner of figure 6. The usefulness eventually moves to the lower right corner and/or to the upper right corner to end up in the upper left corner.

Table II. Comparing different business scenarios.

ITEM	Unit	USD/Unit	Cases where steam is unavailable				Cases where steam is available			
			Case 1	Case 2	Case 3	Case 4	Case 5	Case 6	Case 7	Case 8
Nitrogen			Low nitrogen	High nitrogen			Low nitrogen	High nitrogen		
AOD-melting	Kg	0	10	0	0	10	0	0	0	0
EAF-melting	Kg	0,08	0	0	0	0	10	0	0	10
AOD-Surplus	Kg	0	0	10	10	0	0	0	0	0
Nitrogen	nm3	0,15	0	0	1,25	1,25	0	0	0	0
Oxygen	nm3	0,15	0,625	0,625	0,625	0,625	0	0	0	0
Argon	nm3	1	1,25	1,25	0	0	0	0	0	0
Steam	Kg	0,1	0	0	0	0	1	1	1	1
Cost	USD		1,34	1,34	0,28	0,28	0,9	0,1	0,1	0,9

Comparing the cases cost:

Case 1- Case 5:	0,44	USD benefit for the steam alternative when argon is substituted and extra melting has to be done in the EAF
Case 2- Case 6:	1,24	USD benefit for the steam alternative when argon is substituted and alternative cooling creates surplus production
Case 3- Case 7:	0,18	USD benefit for the steam alternative when nitrogen is substituted and alternative cooling creates surplus production
Case 4- Case 8:	-0,62	USD benefit for the steam when nitrogen is substituted and extra melting has to be done in the EAF. The negative benefit indicates that in this case steam is a bad alternative.

In table III, an attempt is made to estimate the economical impact of using steam in a 1.000.000 ton per year mixed stainless steel production using the presented model. The model must of course be investigated for each particular plant as prices and availability for gases, costs for melting, surplus costs, production size and product split differs significantly from one location to the other. The presented figures however give an indication to the economical potential in converting an AOD to allow for steam-blowing.

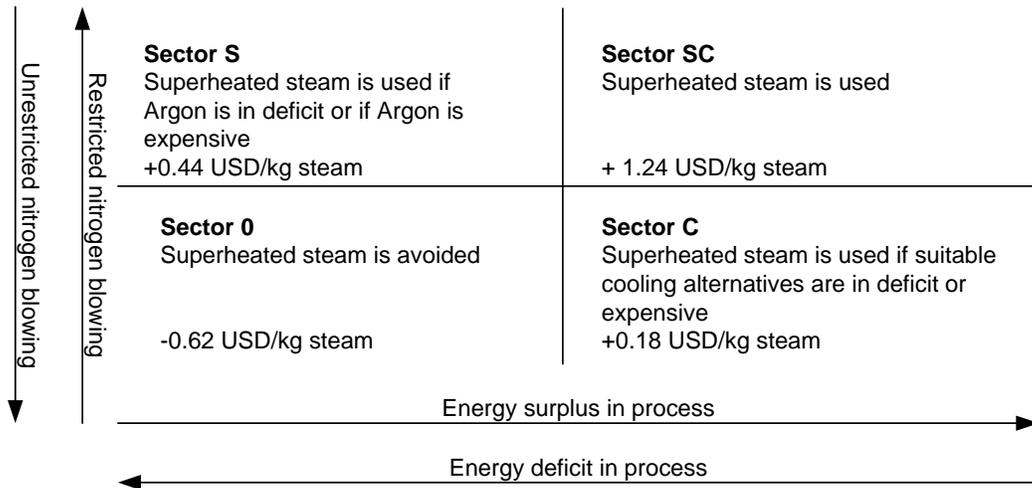


Figure 6. Business model for steam utilization decision making.

From the table it is clear that the best potential for the steam-cooling occurs on those grades where cooling scrap is rare and final nitrogen demand is low. This is typically on high chromium ferritic steels and on super austenitics. But there are also a good potential on standard austenitic grades if the steam is used selectively.

Table III. Results from business model on a 1.000.000 ton per year production case.

Grade	Production	Sector SC	Sector S	Sector C	Benefit
	<i>ton per year</i>	<i>kg steam/ ton</i>	<i>kg steam/ ton</i>	<i>kg steam/ ton</i>	<i>USD</i>
409 etc. low nitrogen	150000		6		396 000
430 etc. low nitrogen	150000	3	6		954 000
304/316 standard	400000	1	2	2	992 000
304/316 low nitrogen	100000	5	5		840 000
Super austenitics	100000	6	6		1 008 000
Duplex	100000			8	144 000
	1000000				4 334 000

Modeling Steam Consumption

In the following sections a number of typical cases for production of a specific steel grade has been simulated to demonstrate that steam has economic potential but also to show how it will be used in the process, and what type of situations are of particular interest for the use of steam.

Initially however the UTCAS converter automation system used to make the simulations is briefly presented.

UTCAS Converter Automation System

UTCAS is an advanced computer system specially designed for the 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 7. It is used for stainless steelmaking in Outokumpus Avesta Works as well as in Acerinox's Columbus Stainless Works.

Process Design

The Process Design 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 economic way with respect to the rules and limitations set by the step sequence definitions. The metallurgical core model is based on Sjöbergs work ¹¹, which in turn can be traced back to the work of Freuhan ¹².

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

- Adjusting gas mixes (oxygen/steam/inert-gas 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.

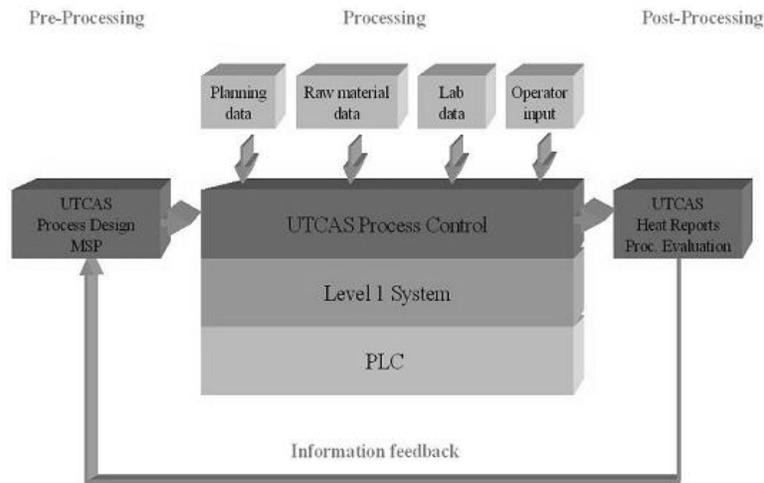


Figure 7. The UTCAS concept for process control and management ⁵.

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 automatic until UTCAS or the operator detects a deviation from the expected results which causes the process plan to be re-optimized and revised.

Simulated Cases

The cases presented below in table IV and the following texts are all refining variations of low carbon low nitrogen 316 suitable for titanium treatment. This grade was chosen because it is common and most steel-makers can relate to it. The steel requires argon blowing throughout the treatment which makes it easy to illustrate the impact of the steam in different situations. Other steels could be just as appropriate to use as example for all or some of the cases.

Table IV. Simulated results for five different practices used to make 316 Ti.

Motivation for steam	FeSi	Scrap	Final mass	O ₂	O ₂	Ar	H ₂ O (g)	Time
	Kg	Kg	Kg	Submerged nm ³	topblown nm ³	nm ³	nm ³	min
Basic AOD-L case	1067	8605	95284	979	1309	2976	0	42:00
Steam prolongs lancing	1054	5468	92175	891	1187	2135	342	37:36
Decreased Ar- consumption	1267	1887	90101	641	1283	1687	988	37:12
Minimised Ar-consumption	2061	3506	90754	521	1343	300	1988	33:24

The start condition for each simulated case is; 80 tons of metal at 1550 °C, 16.55 %Cr, 10.5 %Ni and 2.2 %Mo, 1.6 %C and 0.1 %Si and 900 kg slag. It is assumed that nitrogen usage is restricted in each case. The result for simulations of the different alternatives is presented in table IV.

The main motivation when increasing steam amount in the cases below is to save argon and to meet the desired tap-weight of 90-91 tons. An additional benefit when increasing the steam is that not only does the argon consumption decrease but process time also becomes shorter. This adds to the operating flexibility, plant accessibility and normally shorter process time also corresponds to better refractory economy.

Basic AOD-L Case

Energy is available in surplus in this case which results in 95 tons tap mass- five tons excess of target.

The blowing is made with a surplus of argon during the end of the lance blowing to ensure it can proceed down to 0.3 %C, see figure 8. This is the fastest way and because the desired metal amount is already surpassed it seems to be the most logical alternative.

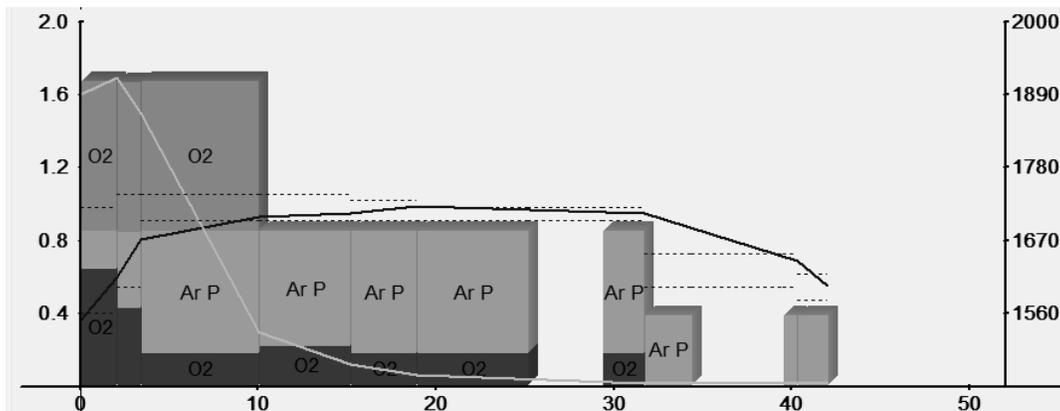


Figure 8. Simulated display of typical AOD-processing of a 316 Ti in a plant operating with top-lance.

Steam Prolongs Lancing

To enable the lance blowing down to 0.3% C without requiring additional scrap, steam is used. This is a very useful strategy as it enables blowing exactly to the critical carbon content without having to fine tune the cooling additions. In particular this is advantageous when scrap is handled in pre-weighed chutes.

This strategy is a simple motivation for steam even though a very limited amount is used. Yet its impact on the process time is significant in this case.

Decreased Ar-consumption

This strategy is a good choice when argon is expensive or if the supply is limited at peak blowing rates. The peak problem is generally related to expansion of steel production without a corresponding expansion of the air separation capacity. This case is showed in figure 9.

By substituting argon with steam during the peak consumption it is possible to maintain stock levels much longer in case the argon is scarce.

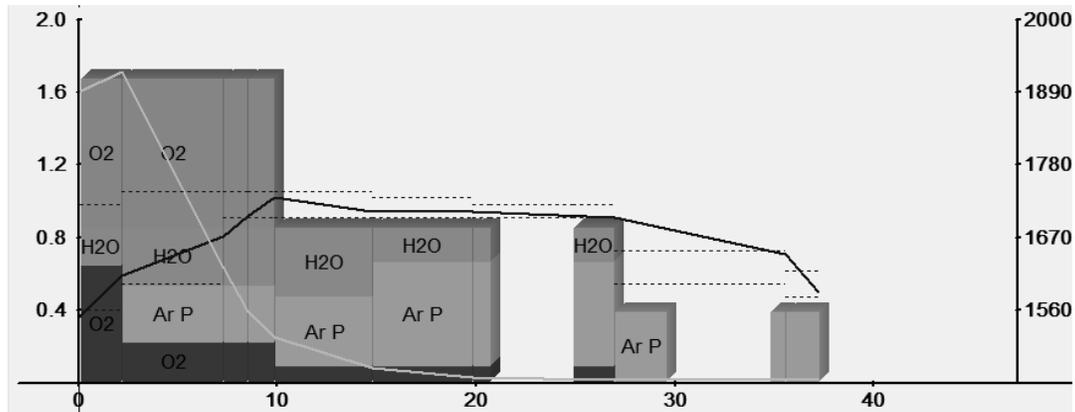


Figure 9. Simulated display of modified AOD-process for a 316 Ti when Argon consumption and peak demand has been decreased by substituting some argon with steam.

Minimizes Ar-consumption

This situation can occur when there is a production disturbance at the air separation plant. It is also a possibility to operate the plant without access to an air separation resource. Only a small amount of argon is necessary during the reduction and the entire consumption can be supplied in liquid form by trucks.

CONCLUSIONS

Steam in stainless steel refining can be motivated by cost savings. In this paper it has been demonstrated that the potential savings are substantial. However it is necessary to fully understand the stainless steel refining process to utilise the benefits.

In the paper it has also been demonstrated how each and every plant can be analyzed to find their potential benefit by using steam as an additional process gas. By the use of UTCAS converter automation system a number of cases have been simulated to show the typical situations where the use of steam is beneficial.

Based on the presented work some conclusions are made:

- Steam blowing capacity is an alternative to increasing gas separation capacity. In a situation where argon supply is less than the demand, installation of steam generation capacity and steam blowing is technically and economically feasible and it requires a much smaller investment than to increase Argon production capacity.
- Steam blowing ability decrease argon cost for two reasons; less argon is consumed and this will decrease the production costs or other contractual obligations related to Argon sourcing; the access to steam might also be an important negotiation lever.
- Steam generation ability decreases the necessary storage capacity and back-up procedures for supply chain disturbances in argon supply. A decrease in Argon supply is no longer stopping production only limiting or changing it.
- Access to the steam improves the ability in reaching the target mass. This is particularly important for plants that operate with tapping mass close to the cranes, ladles or turrets max capacity. For these plants, excess mass caused by cooling requirements leads to over production that cannot be casted by normal procedures. The surplus metal has to be mixed with forthcoming heats or be casted in beds or ingots.
- Access to steam decrease the head-room necessary to avoid surplus production. It is easier to operate close to the weight-size capacity of the plant when there is a cooling method that does not change the metal weight.
- Cooling with steam decrease the need for alloying and expensive scrap additions in the converter.
- Steam decreases the process time for the plant in many situations, which increase the plant flexibility.

These conclusions show that considerable technical, economical and practical advantages are gained by having access to steam blowing capacity. The simple business model, the results from the UTCAS-simulations and the fact that the process is industrially proven, shows that the use of superheated steam has great potential to complement argon and nitrogen as an inert gas in many refining plants.

ACKNOWLEDGMENTS

The help and assistance from my colleagues, Kristina Beskow, Mikael Engholm and Per-Åke Lundström -with suggestions, discussions, proof-reading and editorial advice I appreciate greatly.

REFERENCES

- [1] US Patent 4021233
- [2] US Patent 3252790
- [3] US Patent 3046107
- [4] C. Rick, "Columbus Stainless returns to CLU". *Nordic steel and mining review*. Vol 3/09, p. 54-55.
- [5] C. Rick, M. Engholm: "Control and optimisation of material additions throughout the AOD refining cycle". *Steelsim 09* (2009)
- [6] O. Kubaschewski, and C.B. Alcock (1979). *Metallurgical Thermochemistry*, 5th edition, Pergamon Press, New York.
- [7] J. Chipman, D.A. Corrigan: "Prediction of the Solubility of Nitrogen in Molten Steel". *Transactions of the Metallurgical Society of AIME*. Vol. 233 (1965) No. 7, p. 1249-1252
- [8] M. Weinstein, J.F. Elliott: "Solubility of Hydrogen in Liquid Iron Alloys". *Transactions of the Metallurgical Society of AIME*. Vol. 227 (1963) p. 382-393
- [9] Personal communication with operators and engineers at stainless steel producers.
- [10] R.J. Freuhan, L.J. Martonik: "The Rate of Absorption of Hydrogen into Iron and of Nitrogen into Fe-Cr and Fe-Ni-Cr alloys Containing Sulfur". *METALLURGICAL TRANSACTIONS B*, VOLUME 12B, JUNE 1981, p. 379-384
- [11] P. Sjöberg: "Some aspects on the Scrap Based Production of Stainless Steel". Ph.D.-thesis from the Royal institute of Technology, Stockholm 1995.
- [12] R.J. Freuhan: "Reaction model for the AOD process". *Ironmaking and Steelmaking*. (1976) No. 3. P. 153-158.