



This is an electronic reprint of the original article. This reprint may differ from the original in pagination and typographic detail.

Holappa, Lauri

Historical overview on the development of converter steelmaking from Bessemer to modern practices and future outlook

Published in: Mineral Processing and Extractive Metallurgy: Transactions of the Institute of Mining and Metallurgy

DOI: 10.1080/25726641.2018.1539538

Published: 03/04/2019

Document Version Peer-reviewed accepted author manuscript, also known as Final accepted manuscript or Post-print

Published under the following license: Unspecified

Please cite the original version:

Holappa, L. (2019). Historical overview on the development of converter steelmaking from Bessemer to modern practices and future outlook. *Mineral Processing and Extractive Metallurgy: Transactions of the Institute of Mining and Metallurgy, 128*(1-2), 3-16. https://doi.org/10.1080/25726641.2018.1539538

This material is protected by copyright and other intellectual property rights, and duplication or sale of all or part of any of the repository collections is not permitted, except that material may be duplicated by you for your research use or educational purposes in electronic or print form. You must obtain permission for any other use. Electronic or print copies may not be offered, whether for sale or otherwise to anyone who is not an authorised user.

Historical overview on the development of converter steelmaking from Bessemer to modern practices and future outlook

Lauri Holappa

Aalto University School of Chemical Engineering, Department of Chemical and Metallurgical Engineering, Espoo, Finland

Lauri Holappa, PO Box 16100, FI-00076 AALTO Finland; <u>lauri.holappa@aalto.fi</u> Professor emeritus

Keywords: Converter steelmaking; Bessemer; Thomas; Oxygen converter; Bottom blowing; Hybrid processes; Post combustion; Continuous converting; Future aspects.

Historical overview on the development of converter steelmaking from Bessemer to modern practices and future outlook

Abstract

Converter steelmaking is the main stage in ore-based production using blast furnace hot metal and steel scrap as charge materials. Over 70% of steel is produced via basic oxygen converters today. The converter process was developed in the middle of 19th century by blowing air through pig iron melt for decarburization. The subsequent innovation was basic lining and the Thomas process. The next problem, the switch from air to oxygen was hard and did not succeed on an industrial scale until the 1950s when oxygen blowing via top lance was developed. Oxygen bottom blowing was then solved by applying annular nozzles with hydrocarbon cooling. Current technologies combine benefits of top and bottom blowing in hybrid processes. In this review, the history of converter processes is briefly surveyed. Recent progress and challenges, e.g. better utilisation of post combustion for scrap melting, are discussed. Continuous converting and the future role of converter process are also highlighted.

1. Introduction

The converter process originates from the middle of 19th century when Henry Bessemer set in motion the progress, which has led from air-bottom-blowing converters to current hybrid vessels with combined blowing of oxygen and inert and/or protective gases. The author of this review has highlighted the historical aspects with unconventional rigour. The motivation for this is an exceptional collection of old articles, books and compendia, which were available. As examples, Bessemer's Autobiography, Barracglough's book Steelmaking 1850-1900, Wibergh's lecture compendium, Eketorp's lecture compendia, and the booklet 'One Year LD-Steel' published by Vöest in 1953, are quoted here.

2. Short history of iron and steel making until the middle 19th century

It is generally accepted that the utilisation of iron started in Asia Minor about 2000 BCE (Cobb 2012; Tylecote 1984). There have been findings of earlier iron pieces but they are of meteoritic origin. Archaeological findings have given evidences that ironmaking was discovered by the Hittites in ancient Anatolia, south from the Black Sea. It is possible, that the discovery happened accidentally in connection with copper making, when iron sand was used as flux in copper smelting. Charcoal was well known as fuel for heating and it could reduce iron oxide and form metallic iron lumps. The next invention was that the iron was a potential material for weapons and tools, and its production was started on its own. The historical epoch of the Iron Age, defined as a period when the skill of ironmaking had spread widely, started 1200-1000 BCE. First, the knowledge spread to Eastern Mediterranean region and Europe and somewhat later to Africa, Egypt and to Asia, India and China (Tylecote 1984).

Early primitive furnaces were of bowl type and often constructed in a hillside to exploit natural draught of air. In more advanced furnaces air blast was generated by bellows. The bloomery process governed iron/steel making technology for the next millennium and beyond, known, e.g. as Catalan hearth (Thomas 1999). In these early furnaces, formation of metallic iron took place in the solid state, and the product had low carbon content. There was no need for converting to decrease carbon content by oxidation. Ancient blacksmiths knew from experience how to decarburise or carbonise to the desired final carbon content in their forge furnaces. In the course of time, larger bloomeries were erected and equipped with efficient water-driven bellows. Then temperature inside the hearth could rise too high leading to carbon dissolution into iron, the melting point was reached and the iron bloom melted. The blast furnace was thus accidentally discovered. Towards the end of the Medieval Age blast furnace technology was gradually established in Europe. In China liquid iron was known much earlier, about 200 BCE and in India somewhat later. Liquid iron could be utilized in castings but it was difficult to convert iron into steel. Effective decarburisation methods were not available until the 18th century. To convert liquid cast iron into steel finery methods were developed, like Osmond and German forges, Walloon, Lancashire and Franche-Comté hearths, from the late Middle Ages to the 19th century (Wiborgh 1904). These methods were based on melting of pig iron by combusting charcoal and slow decarburization refining in semi liquid/semi solid state. In the 18th century, more efficient refinery methods were developed. The puddling furnace was a kind of reverberatory furnace. Pig iron was melted by flame from a fireplace, where coal or coke was burnt as fuel. After melting the charge, carbon in the molten iron was oxidized by air by stirring the melt with puddling bars. When the carbon content decreased, the iron solidified and it was gathered by the puddler into a single mass, pulled out and worked under a forge hammer, and then the hot wrought iron would be run through rollers. By using the puddling process, it was possible to produce steel in one stage, faster and with less fuel than with the earlier methods. Another process, crucible steelmaking was developed by clockmaker Benjamin Huntsman in 1740. Cold pig iron was charged with slag-forming flux in small crucibles made of clay and graphite, and then melted by combusting coke. Then low carbon steel was added and melted to get liquid high-carbon steel (e.g. 1% C). The product received was hardenable steel and suitable for tools, mechanical parts etc. Crucible steel remained in a strong position for special grades like tool steels until the first half of 20th century. The aim of the process was actually not in decarburisation but rather in combination of high- and low-carbon metals. The ancient Indian wootz steel was based on a similar principle (Srinivasan & Ranganathan 2004).

3. Invention of converter process

The real breakthrough in large scale steelmaking happened via the development of the converter process by Henry Bessemer in the 1850s. Bessemer was a creative person, who made and patented numerous inventions in different fields. One his invention concerned gun shots. At the time of the Crimean War, spherical shots were being replaced by elongated projectiles. Bessemer devised means of rotating projectiles and made within or on the surface of the projectiles longitudinal passages, which turned tangentially in the front end. When the gun was fired, a small portion of the gases passed up these channels, and emerging as tangential jets made the missile rotate (Bessemer 1989). Actually, the metallurgical problem was not in the projectiles but in the guns. They required a large amount of castable metal with properties comparable with steel. When he made trials in a reverberatory furnace to speed up the process, he blew air through perforations in the firebridge and observed it was possible to convert pig iron into malleable metal without any puddling. He was so convinced of the impact of air-blowing that he took out a patent for the manufacture of cast steel in 1855. Next, he made trials in crucibles charged with 10 lb hot metal by blowing air from the top through a clay pipe (Figure 1a). Then came a converter with six horizontal tuyéres in the bottom and charged with 7 cwt of molten pig iron (about 350 kg, Figure 1b). Bessemer described the first trial: 'All went on quietly for about ten minutes; sparks such as commonly seen when tapping a cupola, accompanied by hot gases, ascended through the opening on the top of the converter, just as I supposed would be the case. But soon after, a rapid change took place, in fact the silicon had been quietly consumed, and the oxygen, next united with the carbon, sent up an ever-increasing stream of sparks and a voluminous white flame. Then followed a succession of mild explosions, throwing molten slags and splashes of metal high up into the air, the apparatus

becoming a veritable volcano in a state of active eruption. --- However in ten minutes more the eruption had ceased, the flame died down, and the process was complete'.





Via these early experiments, Bessemer was able to confirm the main features of the new process: in the first stage, silicon is oxidised and then followed by very fast decarbonisation period. Further observation was, that the process generated so much heat, that no external or internal heat was needed. In spite of the blast of cold air, the temperature of the molten iron increased and it remained molten even when the solidification temperature was increasing with decreasing carbon content. After successful trials at St. Pancras, London, Bessemer presented a paper titled 'The Manufacture of Malleable Iron without Fuel' at the Cheltenham meeting of the British Association on 11th August 1856. Thereafter a wide interest awaked and several plants in Britain started to make trials. However, they led to disaster, as the products were brittle and useless. Gradually it was revealed that the new furnace was unsuitable for

high-P hot metal; Bessemer's own experiments were with low-P pig iron. For the emergence of Bessemer process, the work by Göran F. Göransson in Sweden was essential. He visited Bessemer, became convinced of the new technology and purchased partial rights and installations from Bessemer. First trials were performed in a horizontal, cylindrical converter in 1857 in Edsken, Middle Sweden but without any success. He returned to a fixed furnace and in summer 1858 operation was successful (Granhed 2004). The key revision was that the number and diameter of tuyeres was increased and the air pressure was decreased. The process ran smoothly and faster, and with smaller heat losses. Indeed, the first converters had a fixed construction, which could cause problems in the case of any disruption, as ceasing the blowing caused major damage. Then Bessemer got an idea to mount the converter on axes to be able to keep the tuyéres above the melt during the charging and allow cessation of blowing during the discharge. A pear-shaped converter was charged with molten pig iron; compressed air was blown through bottom tuyéres into the molten metal and silicon and carbon were oxidized and removed from molten iron in 10-20 minutes (Figure 2).





Figure 2. Principal structure of Bessemer converter (left) and a picture of Bessemer's steelworks at Sheffield after 1859 (Bessemer 1989)

There is one more invention and knowhow, which made the converter process applicable in industrial use. When the low-carbon product was tapped from the converter, it had very high oxygen content; i.e. it was undeoxidised, unkilled steel, not of high quality. Robert Mushet remelted defective metal from Bessemer and came up with adding spiegeleisen (cast iron with 5-15%Mn), thus deoxidising the melt and converting it into usable material (Barracglough 1990). Although supported by other innovators, Bessemer's invention was revolutionary, and it influenced the rapid growth of steel production during the next decades. Finally, it should be noted that William Kelly in Kentucky, the United States, had made contemporaneous experiments by air blast in molten pig iron, and could make malleable steel. He also noticed the process was very fast with strong heating effect and he 'proclaimed his discovery to make steel without fuel'. Unfortunately, he was not able to convince the local ironmasters who rejected his idea. Consequently, Kelly got an American patent to his invention only 1857, when Bessemer had been granted an American patent the year before (Habashi 1994).

3.1. Acid versus basic processes

As pointed out earlier, the Bessemer process could not accept hot metal rich in phosphorus. The reason was that the converter had an acidic silica lining, which made it impossible to make basic slag and refine high phosphorus hot metal, common from British as well as continental blast furnaces that time. It was known that phosphorus could be removed by using basic lime-rich slag but that rapidly destroyed the acid lining. The problem was investigated in the 1870s by calcining limestone (CaCO₃), magnesite (MgCO₃) or dolomite (Ca,Mg)CO₃ at high temperature to produce calcia, magnesia or doloma material, which was then pressed into bricks for lining the converter. Problems arose due to the hydration sensitivity of these materials. S. G. Thomas and P. C. Gilchrist, who were cousins, succeeded in developing basic doloma lining, which achieved readiness for industrial application in 1879 (Barracglough 1990). The decisive inventions were dead burning of dolomite at 1200°C and hot tar binder in brick ramming, which gave good mechanical strength and hydration resistance. Metallurgical results of industrial trials were most promising. Hot metal for the Gilchrist-Thomas process could contain up to 3% P. By using lime-rich slag (~50% CaO), phosphorus could be effectively removed into the slag as calcium phosphate. It is noteworthy that most dephosphorisation took place only in the final stage of the blowing; i.e. at low carbon level. In order to reach low P contents, two minutes 'overblow' was continued after the carbon flame had died down. A comparison of the acid and basic processes is shown in Figure 3 (Barth 1942). The new process had another advantage. Due to high phosphorus burden the Thomas slag, which formed in the process, was very rich in calcium phosphate (around 5wt % P in the slag) and was thus a valuable by-product suitable as fertilizer. Basic Thomas converters gradually gained a foothold especially in Central Europe where high-P ores were utilised in larger amounts.



Figure 3. Change of metal composition with blowing time in the acid Bessemer process (left) and in the basic Thomas process (right). Modified from (Barth 1942).

Basic lining was also adopted in other processes, particularly the Open Hearth (OH) or Siemens-Martin (S-M) process developed by Siemens and Martin brothers in the 1860s. According to its main principle, pig iron and scrap were melted in a furnace by a flame exploiting regenerative gas heating. The exhaust gases were used to preheat air and fuel gas prior to combustion and the furnace could achieve sufficiently high temperatures to melt steel. In this process, pig iron was converted into steel by adding scrap and iron oxide or air (later oxygen) into the molten metal bath and the carbon content was reduced by oxidation and dilution. The OH process started as an acid process with acid lining, and then the basic lining and new steelmaking practice were adopted as well. The process had two main differences relative to the Bessemer process: (1) Pig iron and scrap of any composition could be melted in any ratio, and (2) better control of the steel quality was possible. Because of these advantages, the open hearth process became the dominant process over the period 1900-1970 (Figure 4). Typically, big steel plants with blast furnaces were equipped with both converters and open hearths, and eventually even with electric furnaces to have flexibility in steel production.



Figure 4. Share of steel production via different processes from 1860 to 2015 (data based on: Worldsteel 2017; Jalkanen & Holappa 2013).

3.2. Development to oxygen top-blown converters

The Bessemer and Thomas converters represent *pneumatic* steelmaking based on blowing air. However, the central role of oxygen has been understood since the end of 18th century and it was known that air contains only 21 Vol-% oxygen whereas the rest is mostly nitrogen. Bessemer had all these aspects in mind when he patented a 'steelmaking process with oxygen blowing'. However, there were no practical prerequisites to implement the idea. It took around a century to realize an oxygen converter. Blowing air into liquid steel had two major problems, both connected to nitrogen. Blowing nitrogen directly into steel resulted in considerable dissolution, up to 150-200 ppm [N] (Figure 3), which brought harmful effects on steel quality. Large nitrogen volume had also a strong cooling effect thus lowering scrap melting capability. Use of oxygen instead of air was thus more desirable. After Bessemer's era, numerous attempts were made to use oxygen; however, catastrophic wear of the bottom or tuyere area was stated to occur. In the 1920 - 30s large scale production of oxygen gas was established. This made use of oxygen in process industry economically attractive. However, the problem of bottom wear was still unsolved. As a compromise solution, oxygen enriched air was tested up to 30-35% O₂ which seemed to be the limit due to the wear of nozzles and the bottom. Another potential principle was to substitute N₂ for a smaller share of neutral but more efficient protecting gas like CO2 or H2O (steam) and thus allow a higher percentage of O_2 (50:50) in the blowing. Both these gases react with dissolved carbon via endothermic reactions, thus protecting the nozzle area, but at the same time decrease the scrap melting capacity. It was possible to solve the problem of nitrogen but the strong cooling effect remained. Some attempts were made for oxygen bottom blowing in the early 1900s but without success. Finally, the problem was solved by the invention of oxygen top blowing via a water-cooled supersonic lance. In 1939, C.V. Schwartz applied for a patent according to which an oxygen jet was blown down at supersonic rate onto a metal bath entering it deeply (Hauttmann 1953). This did not lead to industrial application. In 1948 the Austrian steel company Vöest was considering enlargement of production. They heard about the experiments by Robert Dürrer and H. Hellbrügge with an inclined jet of pure oxygen on a bath of pig iron in 2 tons vessel in Gerlafingen, Switzerland. Following advice of Dürrer the experts at Vöest began to finalize this idea and started trials, first in a 2 ton converter and in 1950 at a bigger 15-20 t scale. Results were so positive, that planning of a new steel plant was started and the first two 30 ton industrial top-blown converters were put into operation in Linz in 1952 (Hauttmann 1953; Trenkler 1953; Krieger 2003).). The method is known as LD

(originally Linzer Düsenverfahren, but better known as Linz-Donawitz process, according to the plants, which first adopted this technique). Nowadays we commonly call it BOP/BOF (Basic Oxygen Process/Furnace). The LD process rapidly emerged in the 1960s and displaced first most of the old Bessemer and Thomas converters, and later even open hearths had to stand aside - an event accelerated by the progress of electric furnaces (Figure 4).

3.3. Early modifications of BOF process

As the newly developed LD process was not as efficient for dephosphorisation as the old Thomas process, a number of modifications were developed for high phosphorus hot metal. A rotary converter with oxygen lance was developed by Professor Bo Kalling and was installed at Domnarvet, Sweden in 1954. The process was called Kaldo. The inclined vessel could rotate on running rings. Due to rotation, the slag was driven towards the converter wall and oxygen was blown through a water-cooled inclined lance onto the almost bare hot metal surface. The movement of slag and metal resulted in intensive mass and heat transfer between the phases and efficient dephosphorisation was achieved. By using a secondary oxygen lance, a remarkable part of the CO gas formed by carbon oxidation could be post combusted to CO_2 . Exceptionally good heat economy resulted, due to post-combustion, and up to 50 % scrap ratio could be reached (Michaelis 1979). A number of Kaldo converters were installed in different countries but when the raw material basis turned to low phosphorus concentrates the need for special converters gradually disappeared. In spite of the mentioned metallurgical advantages, Kaldo could not compete with common LD due to its mechanical complexity and more intensive wear of furnace lining caused by rotation of the vessel. The last Kaldos were closed towards the end of the 1970s. Kaldo-type converters were adopted in non-ferrous metallurgy for smelting or converting of matte containing

copper, nickel or lead and for treatment of secondary raw materials; e.g. dusts since the 1960s. Recently, it has found applications for electric and electronic waste (WEEE) processing. The process is known as TBRC (Top-Blown Rotary Converter). A comparable process ROTOR was developed in Germany at Oberhausen in the late 1950s (Graef et al. 1957). Rotor was a long cylindrical furnace mounted horizontally on axes and provided with two lances, one submerged lance to oxidize carbon and other impurities, and the second lance to post-combust CO into CO₂ inside the reactor and utilize the heat for scrap melting. A few reactors, each of 100 tons capacity were installed in Germany, South Africa and U.K. in 1958-1961. The method had the advantage of flexibility, but it suffered from similar drawbacks as Kaldo; i.e. mechanical complexity and refractory wear, which meant high costs. A further concept for a rotating converter was Rotovert, a vertical vessel with double lances. It was tested at small scale in 1960/70s (Ramacciotti et al. 1971).

As high-P hot metal was still common in the 1950s, several modifications of LD process were developed, for instance LD-AC process at ARBED/Dudelange and OLP process by IRSID, first applied at Sacilor (Michaelis 1979, Mousel 1979). Both used a special lance with combined oxygen - lime injection. The blowing took place typically in two stages; first most of the phosphorus was oxidised into slag, which was then tapped and utilised as a fertilizer due to its high P content, comparable with traditional Thomas slag. Only a part of the carbon was oxidised during the first stage, and the oxygen blow was continued in the second stage to attain the final low carbon level.

3.4. Oxygen bottom blowing

In spite of special oxygen converters, many air blown Thomas converters survived through 1960-70 converting high-P hot metal. From the 1950s Savard and R. Lee at

L'Air Liquid in Canada tried to develop oxygen bottom blowing (Mackey & Brimacombe 1992). Moderate success was attained with high pressure (4825 kPa) nozzles when a protective accretion or mushroom was discovered to form at the tip of the bottom injector. The cooling effect is based on Joule-Thompson expansion. Savard and Lee were granted a patent in 1958 for their oxygen steel refining process. High pressure oxygen in tandem with high temperature was a deterrent combination, and investigations were continued to find another cooling technique and mechanism. A successful concept was to shield the oxygen jet with an inert gas, but better yet, an oxygen-getter gas that would displace the highly exothermic metal oxidation reaction away from the tip of the injectors. The solution was an annular nozzle, via which oxygen was blown through the inner pipe and protecting and cooling hydrocarbons, methane and propane were injected through the outer pipe as endothermic shrouding gas (Savard & Lee 1966, Knüppel et al 1972). The first bottom blown oxygen converter was successfully commissioned at Maxhütte, Germany in 1967 (Brotzmann 1979). The new process was adopted by retrofitting old Thomas converters as well as in new greenfield plants. The process was called OBM (Oxygen-Bottom-Maxhütte) according to the first converter. A similar process but applying liquid oil as protecting medium was developed by Creusot-Loire Enterprises in France in co-operation with the company Sollac, which had several Thomas converters in operation still until the early 1970s (Maubon 1979). In the United States the bottom-blown process was called Q-BOP, quiet BOP. The share of bottom blown converters is today approximately 10% of the overall capacity of converters. A similar principle of concentric nozzles was applied also in side-blown AOD converters for stainless steelmaking, where inert argon gas is used as surrounding cooling gas, but its ratio to O₂ is much higher as its role is, at the same time to reduce the partial pressure of CO and thus promote the decarburization

reaction (Krivsky 1973, Patil et al. 1998). The first commercial converter started operation at Joslyn Steel in 1968. Another converter process designed for stainless steelmaking is CLU (Creusot-Loire-Uddeholm) which was developed in early 1970. In this process, expensive argon was replaced by superheated steam i.e. water vapour which is an efficient cooling medium when it dissociates into hydrogen and oxygen. At the blow-end, steam was switched to argon to purge most of the dissolved hydrogen. The CLU process had a limited distribution, for stainless and for ferroalloys refining in South Africa (Bouver 1992).

3.5. Hybrid converters – modern technologies

A comparison between the OBM and BOP processes reveals clear differences; bottom blowing leads to near-to-equilibrium results, whereas after top blowing the slag and the metal bath both are significantly over-oxidized. The reason is self-evident: bottom blowing induces intensive stirring and good mixing, whereas top blown oxygen jet has weaker and relatively local stirring effect leaving the most of the steel bath quite quiescent. On the other hand, bottom blowing represents a more complicated technique, with extra expense and risk, compared to lance blowing. Hence, the combination of the benefits of both processes into one seemed optimal. Numerous combined processes arose since the middle 1970s to 1980s. Most of these were based on the LD process with additional inert gas bottom blowing. Today, a great majority of converters are such hybrid processes. The estimated stirring effect of the bottom gas for different processes is illustrated in Figure 5, where mixing time is presented as a function of bottom gas flow rate (Chatterjee et al. 1984).



Figure 5. Effect of bottom gas flow rate on the bath mixing time in different converter processes (redrawn from Chatterjee et al. 1984).

The advantages of combined blowing compared with pure top blowing are (Chatterjee et al. 1984):

- acceleration of blowing efficiency owing to strongly intensified melt stirring;
- smaller over-oxidation of slag; lower iron oxide content and better iron yield;
- lower splashing and spitting of slag; better iron yield;
- increased refractory lining life by avoiding over-heated, iron oxide rich slag;
- increased accuracy in end composition and temperature due to better homogeneity; and
- reduced consumption of deoxidants and better yield in alloying.

Various converter technologies are collected in Table I starting from the original LD process, proceeding to LD-type processes with inert gas bottom stirring, further to oxygen-top + oxygen-bottom processes and plain bottom blowing processes. Further,

some allothermal processes were included with extra combustion to increase scrap

melting capacity, and finally special converter technologies for stainless steel making.

			Т	op	Bottom blowing								
M ·	D	Dural	blov	ving	0		Car	т	NT + /	00	0.1	0 1	C 4.
Main category	Process	Developer	O_2	$O_2 + C_2O$	O_2	$O_2 + C_2 O_2$	Gaseous CH	Liquid C. H	$N_2 + /or$ Δr	CO_2	Coke	Coal	Steam
Ton	LD	Vöest-Alnine	+	CaU		CaU	Umrn	Umi in	A1				
blowing	LD-AC	Arbed-CRM	+	+									
	AOR	Inland Steel -	+	$\Omega_2 +$									
	AOD	Union Carbide		Ar									
Ton +	ID-S	Vöest-Alpine	+						+				
bottom	ID-KG	Kawasaki	+						+				
blowing I		Nippon-Kokan	+						+				
	LD-AD		+						+				
	TRM	Thyssen	+						+				
	M_TRI	Mannesmann	+						+				
		Arbad	т 						г 				
	LDE NK CP	Ninnon Kolon	+ +						+ +				
	ID CI	Nippon-Kokan							+ +				
Tore	LD-CL	Nippoli-Kokali			(1)				+				
1 op + bottom	LD-OIB		+		(+)				+	+			
blowing II	LD-CB	Nippon-Kokan	+		+				+	+			
	LD-SIB	Sumitomo	+		+				+	+			
T	LD-OB	Nippon Steel	+		+		+		+				
1 op + bottom	LD-HC	Maxhütte	+	+	+		+		+				
blowing III	K-OBM	Klöckner-	+		+		+	+	+				
0	K-BOP	Kawasaki	+			+	+	+	+				
Bottom	ORM/	Maxhütte/			+	+	+	+	+		1		
blowing	Q-BOP	US-Steel				'							
0	LWS	Creusot-Loire				+	+	+	+				
Allothermal	KMS	Klöckner-			+	+	+	+			+	+	
		Maxhütte											
processes	KS	Klöckner-			+	+	+	+			+	+	
	Z-ROP	Zansih	+								+	+	
Stainless &	AOD	Union Carbide	+		+				+			-	
high alloy		Lindé Division											
steels													
converting	VOD	Witten	+						+				
	(VODC)	(Thyssen)			+								
	CLU	- Uddeholm			+				+				Ŧ
	K-OBM-	Klöckner-	+			+	+	+				+	
	S	Maxhütte											

 Table I Collection of Converter Processes (Revised from Jalkanen & Holappa 2013).

4. Heat balance and scrap melting capacity in converters

In general, in oxygen converting processes no external energy is required as much heat is released when the hot metal carbon, usually between 4 to 4.5wt%, is oxidized to contents between 1 and 0.02wt%C depending on the final carbon target. Even the hot metal silicon (typically 0.3-0.5%) is oxidized via strongly exothermic reaction. The other components (Mn, Ti, V, P) are partly oxidized and bound in the slag which is formed by the added lime and solid or liquid oxides generated in oxidation reactions. Additionally some iron (as the dominant component) is oxidized and participates in slag formation. Also refractory lining material dissolves into slag in some amount which can be recognized as increased MgO-content in the slag. An example of the changes of steel and slag compositions during a blow are shown in Figure 6. Depending on the hot metal chemistry and temperature at charging as well as the aimed steel targets there is a significant surplus heat which must be compensated by cooling with recycled steel (scrap), the amount being typically 15-25% of the total charge weight. For temperature adjustment during the blowing period smaller additions can be used; e.g. iron ore/pellets for cooling and FeSi for heating, respectively. An example of a converter heat balance is given in Figure 6 (left). In the input column, reaction heat shows the exploitable enthalpy of reactions which is then converted to sensible heat of steel, slag and off-gas in the output column. Most of the reaction heat is consumed in melting of the charged scrap, and heating the iron/steel melt to the final aim temperature, 1923-1973 K (1650-1700 °C). Off-gases take the next biggest fraction of the heat. Then some heat goes to slag formation and heating as well as in heat losses.



Figure 6. Heat balance calculated for an 111t heat. Reference state 25°C. Input: hot metal 97t (T=1595 K; 4.4%C, 0.35%Si, 0.31%Mn, 0.12%V); scrap 20t, lime 4t, O₂ Fig5000m³. Output: steel 111 t (T=1652°C; 0.09%C, 0.23%Mn); slag 6.2 t (60%CaO, 15.4%FeO, 15.3%SiO₂, 4.6%MnO); off-gas 90%CO, 10%CO₂, T=1610°C) (Revised from Holappa & Jalkanen 2003). Figure right: An example of metal and slag compositions during a BOF blow (Holappa & Jalkanen 2003).

The interest of a BOF steelmaker to increase scrap melting capacity depends on the availability, price and quality of scrap. Table 2 highlights the global situation. In the United States, scrap availability has been propitious and the share of electric steelmaking is amazingly high, about 2/3 of the all steel. In EU countries, the BOF/EF ratio is 60/40. Even BOF plants tend to maximise their scrap usage. By contrast, the situation is different in Eastern Asia, China, Japan and South Korea, where the BF-BOF (OBC) steelmaking route is dominant. As there is a shortage of scrap, there is no incentive to increase the scrap rate in converters. In China, the ratio is up to 94/6 today but in the longer run the situation will change resulting in both growth of EF production and increasing scrap usage in converters (Haslehner et al 2015).

Table 2. Total steel production and distribution by process at biggest steel-producing countries, European Union and World in 2016. OBC=Oxygen-blown Converter;

Region/Country	Total steel, million tons	OBC, %	EF, %
China	807	94	6
Japan	105	77	23
India	95	43	57
South Korea	68	70	30
Russia	71	67	31
EU (28)	166	60	40
United States	79	33	67
World	1626	74	26

EF=electric furnace (Worldsteel 2017).

A further aspect comes from circumstances inside an integrated plant; for example disruptions in hot metal production due to maintenance or renovation actions which cause temporary interest to increase scrap ratio in converters. Allothermal processes (Table I) give a solution to this problem. By combusting coal, coke or hydrocarbons inside the converter and utilizing oxygen lance the scrap ratio can be increased to 30-40% (KMS, Fritz & Gebert 2005). Even 100% solid charge is possible with special technologies like KS which was commissioned on the 125 t scale at Klöckner Werke AG Georgsmarienhütte in 1983 ((Geck and Chitil 1986). There solid charge could be melted and refined in 111 min.

4.1. Heat content of off-gas and post-combustion

As seen in Figure 6 the converter off-gas has a remarkable heat content, partly as sensible heat and partly as chemical heat of the unreacted CO gas. This heat rests on the fact that oxidation of CO to CO₂ generates approximately double the amount of heat compared to primary oxidation of carbon to CO. In a conventional BOF, the off-gas inside the converter contains about 90% CO and 10% CO₂, the ratio changing and depending on the stage of the blow as well as process conditions (lance height, additions, slag conditions, bottom stirring and leakage air). In Figure 7, an example of measured CO and CO₂ contents at the converter mouth is presented (Lassila et al. 2004). Gas samples were taken by a water ejector sampler through a tube about 50 cm inside the converter mouth. In spite of the water separation before the IR-analyser, some water vapour and air could not be avoided in the sample and hence the sum %(CO+CO₂) \approx 80. During the first 2-3 min the sum is much lower and the 'apparent PCR' quite high due to strong distribution of O₂ to oxidation of Si, Mn and Fe and less to carbon oxidation. During the main carbon oxidation period the rate is quite constant and the share of CO₂ and PCR are low. Towards the end of the blow, when carbon content has fallen under 0.2%, CO formation is decelerating, and PCR is increasing due to leakage air and the influence of 'FeO' in the slag.



Figure 7. Measured carbon oxides and PCR in off-gas inside a 55 ton BOF (redrawn from Lassila et al. 2004)

In general, the post combustion ratio is expressed by PCR (%) = $100(\%CO_2+\%H_2O)/(\%CO + \%H_2+\%CO_2+\%H_2O)$. In the example case, H₂O and H₂ were very low and not analysed. As known in literature (Sandlöbes et al. 2011) and seen in Figure 7, the PCR value is quite small during the main decarburisation period, in the range 5-20% with the mean value around 10%. Hence, quite a small fraction of the potential combustion heat is utilised inside the converter. If there is an air gap between the converter and the hood, the off-gas flow acts like an ejector and sucks surrounding air, then combusting CO into CO₂ inside the hood and the boiler, where the heat is recovered in a waste heat boiler, generating high pressure steam. Heat efficiency, however suffers from the surplus air (N₂), typically 2-3 times, which dilutes and cools the off-gas line. In such a case, the sensible heat of the off-gas is first recovered in a waste heat boiler, then cleaned, stored in gas tanks, mixed with other by-product gases from coke oven and blast furnaces, and finally

used as fuel for heating purposes, in a power station etc. Non-combustion methods can recover about 70% of the chemical and sensible heat. Typically, the very first and last batches are cut-off from entering the gas storage due to their higher PCR, low calorific value and for safety reasons. The third and most fascinating method to exploit off-gas would be, however, post combustion inside the converter and direct utilisation in melting extra scrap. As stated, some post combustion takes place in normal BOFs in the oxygen jet and its vicinity. Part of the formed CO_2 can be reduced to CO via decombustion reaction with dissolved carbon. The gross effect depends on whether the blow is 'hard' or 'soft' (Hirai et al. 1987). In order to increase PCR in a remarkable and controllable way, secondary oxygen blow has been applied. Special post combustion lances had already been used in Kaldo and Rotor converters in the 1950s. For modern top-blown converters special lances have been developed also (Takashiba 1989, Hamagami et al. 1992, Umezawa 1992; ECSC 2002; Boom 2003).). Extra nozzles for secondary oxygen were added in the oxygen lance to an upper level above the tip nozzles or by providing the lance with two independent oxygen flows. Such 'double flow lance' with two independent oxygen blow systems enables better control of post combustion. As the combustion takes place in the slag phase, the temperature increases, slag becomes more fluid, lime dissolution accelerates, slopping and skull formation tend to decrease and blowing time decreases.

In bottom-blowing converters the lance can be used both for decarburisation and post combustion and has more freedom to operate; e.g., it has been used to remove mouth skull (Farrand et al. 1992, Takahashi et al. 1990, Ibaraki et al. 1995, Dubois et al. 2000). Except for scrap melting post combustion has been intensively studied in smelting reduction reactors like the Japanese DIOS, American AISI Direct Steelmaking program and European Jupiter and CCF initiatives (Ibaraki 1995, Aukrust 1994, Abildgaard et al.

1997). The phenomena in post combustion and influencing factors were modelled too (Gaye et al. 1990, Zhang & Oeters 1991, Gou et al. 1992, Höfer et al. 1992; Fruehan & Matway 2005). Experimental results and modelling have shown that apart from post combustion ratio PCR, another factor, heat transfer efficiency HTE is very crucial. HTE (in percentage) is the heat absorbed into the steel bath from the total heat generated in post combustion. In order to maximise scrap melting capacity both PCR and HTE should be high. Measured PCR values are typically in the range 20-50% and HTE values 50-85%. Unfortunately, the relations are somewhat reverse: higher PCR is partly eliminated by lower HTE. High PCR means high oxidation state in the upper part of the converter resulting in high 'FeO' in slag and bigger iron losses. The problem is how to effectively transfer the post combustion heat to the slag and especially to the iron bath instead of leaving the vessel with off-gas. An efficient mechanism for heat transfer is via the iron droplets, which are ejected from the bulk metal to the foaming slag (actually a slag/metal/gas emulsion), and then descend back to the bulk metal. This circulation has been clearly verified in smelting reduction in converter type reactors with post combustion. As post combustion provides more oxidizing conditions in the slag via O₂ blowing and CO₂ formation, it also intensifies reactions with iron droplets. As a consequence, carbon dioxide is partly reduced back to carbon monoxide. The combination of high PCR and low HTE is not desirable as the off-gas temperature rises too high and will cause thermal load to converter refractories, to the hood and the off gas line. It is evident that these factors should be compromised case-specifically for each converter. A rough evaluation shows that by raising the post combustion ratio from 10 to 20%, scrap melting capacity would increase with 30 kg /t steel, steel production would increase with 3%, respectively, and CO₂ emissions decrease with 60 kg/t steel.

5. Discussion on future - Some brave old and new ideas

The main outlines of the development of converter process since Bessemer until today were discussed above. Some aspects have, however rested aside but are worth of some scrutiny: Why is converting still a batch process? and Is converting necessary in future steelmaking?

5.1 Continuous converting

The main goal of converter process is to decarburise BF hot metal into low carbon steel. Converting is a batch process but blast furnace is a continuous reactor. Even hot metal tapping can be continuous, as is done in very big BFs today. Thereafter the subsequent hot metal treatments and converting are batch processes. Nowadays a batch or heat is made in 40 min approximately. Why not continuous converting? The idea was awaken in 1960s by several research groups e.g. in France, Australia, U.K., U.S. and Japan (Berthet et al., Eketorp, Goss & Blough, Nakagawa et al., Worner & Baker 1971; Rhydderch 1967, Davies et al. 1967). The French process was developed at IRSID research station in 1960-70s (Berthet et al. 1971). The reactor was divided into two compartments, in the first one carbon rich hot metal was fed in and blown with oxygen (Figure 8). Lime was added for slag formation. Then the steel-slag-gas emulsion reached a sill over which it was flowing to the second compartment, a kind of settler or decanting vessel to separate metal from slag. The decanting vessel was equipped with deslagging opening and steel was discharged via a siphon system. The process was successfully tested in pilot scale (10 t/h) and the following advances were reported:

- Lighter investment costs compared with conventional BOF with the same capacity due to smaller scale in all equipment due to continuous operation
- Flexible operation with high iron yield, simple maintenance

• Easy and continuous recovery of off-gas in continuous operation without breaks under atmosphere

Even and high steel quality, good dephosphorisation and end carbon control In general, the main metallurgical problem in continuous steelmaking is how to avoid back-mixing of two zones with totally different carbon content and oxygen potential (Figure 8 left) - the carbon-rich metal near the inlet and the refined low carbon steel. In the IRSID process, this was solved by performing decarburisation in the first compartment and by utilizing gas generation as a pump to transfer decarburised steel over the sill to the second chamber. Several other concepts have been examined. The WORCRA process, initiated in Australia at Broken Hill and tested at Mefos Lulea in early 1970s, used counter current metal/slag flows in a long L-shape launder for refining (Worner & Baker 1971, Brooks, Ross & Worner 1997). In a Japanese NRIM process, steel ran through a multi-stage, cascade type furnace by gravity flow (Nakagawa et al. 1971). Electromagnetic transportation of steel was applied to achieve counter current flow for decarburisation under oxygen top-blow in a tilted runner (Steinmetz 1971). The steel flowed uphill and the slag downhill in the tilted channel. Lime was co-injected to improve dephosphorization. A different principle, spray steelmaking, was introduced by BISRA. The hot metal stream was dispersed into tiny droplets by direct impingement of O₂ blown into the metal stream under the casting nozzle (Figure 8 right; Davies et al. 1967; Rhydderch 1967). The decarburisation reaction is extremely rapid but on the other hand the mass of steel treated per time unit is quite small. Comparable tests were performed at Vöest in Austria in a horizontal spray reactor with side-blown oxygen jets (Steinmetz 1971).



Figure 8. Two examples of continuous converting reactors: IRSID furnace (left) and spray refining by BISRA (right). Revised from (Zimmermann & Günther 1975).

All these methods and several others were tested at pilot or semi-industrial scale and they work metallurgically. But there are some evident drawbacks. As discussed earlier, a general trend is to maximise the scrap melting capability. In the case of a continuous process, scrap feeding should be continuous, it should melt rapidly and distribute evenly in the liquid metal. It is evident, that for practical and thermal reasons the size, shape and amount of scrap are severely limited by the short time allowed for melting. Also such long reactors must have a poorer thermal efficiency because of higher heat losses due to the unfavourable volume/area ratio compared to batch converters. A continuous process is tardy in reacting to rapid changes in the analysis requirements; e.g., endcarbon content, due to the continuity of the material flow. Greater refractory wear was also reported as a potential disadvantage of continuous converting. The volume/area ratio of the reactor, hot temperatures, thermal shocks, high fluid velocities and high FeO content in slag are such influencing factors.

In the 1970s, modern converter processes were still new and intensive development work was focussed on the field. Continuous processes seemed to be an alternative. Finally, none was ever industrialized due to several uncertainties. Today, our knowledge of metallurgical factors of the process, refractory materials, continuous control devices etc. are on much higher level than 50 years ago. That would help in eventual new start of continuous processes. Will continuous converting get its renaissance?

5.2. Is converting necessary in steel production?

In the current global situation over 70% of steel is based on iron ore, reduction in blast furnace into hot metal and then converting into steel. Although the role of recycled steel will more than double by the year 2050 the ore-based route will evidently keep its current volume (Haslehner et al. 2015). Eventual new ironmaking technologies like smelting reduction would use coal and the product would be high carbon hot metal; thus no change in converting would be needed. On the contrary, direct reduction mainly uses natural gas, DRI has low carbon content and its normal processing is via electric furnace; i.e. no converter. However, there are no signs that DR will replace BF significantly, although it has lower CO₂ emissions. Professor Sven Eketorp at KTH Stockholm contemplated about 50 years ago the concept of making iron & steel based on the classical Ellingham diagram (oxygen potential vs. temperature) (Figure 9; Eketorp 1983). First, when iron oxide is gradually reduced in BF (Line A-A₁-A₂-A₃) into hot metal, it becomes carbon saturated and represents very low oxygen potential in point B. Next it is converted to crude steel with much higher oxygen potential and temperature (Line B_1 - B_2 -C). Thereafter the steel is deoxidized (e.g., with silicon or aluminium) to much lower oxygen potential again (Point D). Eketorp asked in the question: Is this reasonable and necessary? Why we don't go all the time in the same direction – directly or step by step? Our ancestors, ancient blacksmiths actually did so in their bloomeries and forging furnaces. They even 'invented' the circular economy; steel was so invaluable that nothing was wasted, but all remanufactured.



Figure 9. Oxygen potential, Ellingham diagram for the essential reactions in ironmaking – steelmaking. Line from A to B represent the Blast Furnace process, from B to B_1 hot metal treatment, from B_2 to C converter process and from C to D deoxidation. Redrawn according to Eketorp 1983.

6. Concluding remarks

The over 160 years history of steel converter process had a few big leaps, first the breakthrough innovations of Bessemer and Thomas, then the solutions for oxygen blowing, and finally, the combinations of different techniques in hybrid processes in order to optimize the functions of converter in the production line. This overview has revealed the main line of the development but also numerous bypaths, which tell us about deviating circumstances or prevailing problems such as high-P hot metal and

delayed industrial production of oxygen. Even today, there are plenty of process variants owing to different frameworks but also reflecting innovativeness and necessity for continuous development. This is really demanded as the role of the converter process will change in the future as the circular economy gains ground in the steel industry.

References

Abildgaard, O., Y. de Lassat, G. Malgarini, M. Mirabile, C. Borgianni, A. Poos, P. Vannson, R. Steffen, B. Welbourn. 1997. European direct steel feasibility study, European Commission, EUR 17824, Brussels.

Aukrust E. 1994. AISI Direct Steelmaking Program. Final Technical Report. DOE/ID/12847-7 (DE94017940); pp. 155.

Barracglough RF. 1990. Steelmaking 1850-1900. The Institute of Metals, London Barth O. 1942. Metallurgian oppikirja – osa 2 (Textbook on Metallurgy, Part 2 Ironmaking and steelmaking). Otava, 1st Edition 1942; p. 272.

Berthet A. Krug JC. Rouanet J. Vayssiere P. 1971. The Industrial Development of IRSID Continuous Steelmaking Process. In: Proceedings of International Conference on the Science and Technology of Iron and Steel. Tokyo, Sept. 7-11, 1970. Part I, p. 272-277.

Bessemer H. 1989. Sir Henry Bessemer, F.R.S. An Autobiography. The Institute of Metals, London. First printed at The Bedford Press, 20-21, Bedfordbury Strand, London WC, 1905.

Boom, R.: Mastering the heat in the Fe-C-O converter: Evolution of process control in fifty years of oxygen steelmaking. Proceedings 4th European Oxygen Steelmaking Conference, 12 - 15 May 2003, Graz, Austria, p. 19 – 37.

Bouver PHF. 1992. Operating and Marketing Results of the Production of Intermediatecarbon Ferrochromium in a CLU Converter. INFACON 6. Proceedings of the 6th International Ferroalloys Conferenge, Capetown. Volume I, SAIMM, p.119-122. Brooks GA. Ross NG. Worner HK.1997. Continuous steelmaking: A Balance between Intensity and Refining. AIST Steelmaking Conf. Proceedings; p. 631-636. Brotzmann K. Basic Oxygen Steelmaking – A New Technology Emerges? p. 41, The Metals Society, London, 1979

Chatterjee A. Marique C. Nilles P.1984. Fundamentals of steelmaking metallurgy. Ironmaking and steelmaking. Vol 11, No 3; 117-131.

Cobb HM. (Ed.) 2012, Dictionary of Metals, Appendix I: Metals History Timeline, ASM International, Materials Park, OH, USA, 304.

Davies DRG. Rhydderch MJ. Shaw LJ. 1967. Spray Steelmaking at Millom, Journal of Iron and Steel Institute, p. 810-813.

Dubois CA. Bosquet JP. Chapellier P. Didry G. Mailhan JC. Grisvard C. Huber JC. 2000. Startup of a post-combustion lance at Sollac Lorraine. EOSC'00, 3rd European Oxygen Steelmaking Conference Proceedings, 30/11/2000 - 1/12/2000, Birmingham U.K.

ECSC. 2002. Research project "Development of a combined post-combustion model (CPM) for smelting reduction processes", ECSC 7210-AA/419, 1994-1997.

Eketorp S. 1971. Continuous Iron- and Steelmaking – Fundamentals and Technical

Possibilities. In: Proceedings of International Conference on the Science and

Technology of Iron and Steel. Tokyo, Sept. 7-11, 1970. Part I, p. 282-287.

Eketorp S. 1983. Process Metallurgy – discussions of present systems and their future possibilities. Part 1. Compendium of lectures at the Beijing University of Iron and Steel Technology. Sept.– Oct. 1983. Royal Institute of Technology, Stockholm.

Farrand BL. Wood JE. Goetz FJ. 1992. Post combustion trials at Dofasco's KOBM furnace. In: 75 Steelmaking Conference Proceedings. Toronto Canada. Iron & Steel Society; p. 173-179.

Fritz E, Gebert W. 2005. Milestones and Challenges in Oxygen Steelmaking. Canadian Metallurgical Quarterly, Vol 44, No 2 p. 249-260.

Fruehan RJ. Matway RJ. 2005. Optimization of Post Combustion in Steelmaking. Final Report. AISI/DOE Technology Roadmap Program; pp. 24.

Gaye H. Grosjean JC. Huin D. Roth JL. Zbaczyniak Y. 1990. Studies on postcombustion in an oxygen converter: mechanisms and operations, 3rd international

Oxygen Steelmaking Congress, May 15-17th, London.

Geck H-G. Chitil M. 1986. Development of the Klöckner steel production process.

Contract No. 7210-CB/101. Final Report EUR 9814. Published 1996-08-02 CD-NA-09-814-EN-C. p. 28.

Goss NP. Blough AK. Continuous Steel Making in Rotary Reactor System. In:

Proceedings of International Conference on the Science and Technology of Iron and

Steel. Tokyo, Sept. 7-11, 1970. Part I, p. 287289.-277.

Gou H. Irons GA. Lu WK. 1992. Mathematical modelling of post-combustion in

Dofasco's K-OBM; 75th Steelmaking Conf. April 5-8, Toronto, p. 181-185.

Graef R, Dick W, von Bogdandy L. 1957. Rotor steelmaking process. Journal of Metals, Vol.9 No. 11, p. 1135-39.

Granhed S. 2004. Bessemer och Thomasprocesserna; in: Järn- och stålframställning – Utvecklingen i Sverige 1850 till 2000. Del 2. Jernkontorets bergshistoriska skriftserie 41.

Habashi F. 1994. A History of Metallurgy. Métallurgie Extractive Québec, Enr. Canada

Hamagami K. Gotoh S. Asaho R. Kuga M. 1992. Operational results of bottom blown converter with post-combustion lance; 18th OBM/Q-BOP Meeting, Salzburg, September 14-17.

Haslehner R. Stelter B. Osio N. 2015. Steel as a Model for a Sustainable Metal Industry in 2050. October 07, 2015. Categories: Industrial Products & Processes, Sustainability. In: https://www.bcgperspectives.com/content/articles/metals-mining-sustainabilitysteel-as-model-for-sustainable-metal-industry-2050/

Hauttmann HF. 1953. Properties of LD-Steels; in: One Year LD-Steel. Vöest 1953. VUB, Innsbruck-Linz; p. 11-15.

Hirai M. Tsujino R. Mukai T. Harada T. Omori M. 1987. Mechanism of post
combustion in the converter. Trans. Iron & Steel Institute of Japan. 27; p. 805-813.
Holappa L. Jalkanen H. 2003. Copper and steel converting – A critical comparison.
Yazawa Int. Symposium on Metallurgical and Materials Processing, Principles and
Technologies, TMS. vol. 2: High-temperature Metals Production, San Diego, CA,
March 2-6, p. 401-416.

Höfer F. Patel P. Selenz HJ. 1992. Fundamentals of post-combustion in steelmaking vessels. Steel research, Vol. 63, No. 4, p. 172-178.

Ibaraki T. Yamauchi M. Matsuo M. Katayama H. 1995. Experimental operation of smelting reduction with a 100-t smelter. II. Post-combustion and dust; I&SM, March 1995, p. 91-98.

Jalkanen H. Holappa L. 2013. Converter Steelmaking. In S. Seetharaman, (Ed.), Treatise on Process Metallurgy, Vol.3: Industrial Processes, Part 1 Ferrous Process Metallurgy; L. Holappa, (Ed.); p. 223-270.

Knuppel H. Brotzmann K. Fassbieder HG. Savard G. and Lee R. 1972. Method for Refining Pig Iron into Steel, U.S. Patent, No. 3706549, 19 December 1972. Krieger W. 2003. 50 Years LD Steelmaking – 50 Years of Innovation. In: Proc. 4th European Oxygen Steelmaking Conference. Graz, Austria 12-15 May 2003; p. 3-17. Krivsky WA. 1973. The Linde argon-oxygen process for stainless steel; A case study of major innovation in a basic industry. Metall. Trans., 4; p. 1439-1447.

Lassila I. Holappa L. Valovirta E. 2004. Investigation on post combustion phenomena in BOF by in-situ gas analysis. Scanmet II, 2nd Int. Conf. On Process Development in Iron and Steelmaking, Luleå, Sweden, June 6-8, 2004; p. 225-232.

Mackey PJ. Brimacombe JK. 1992. Solid-Liquid and Gas-liquid Interactions in a Bathsmelting Reactor. Proc. Savard/Lee International Symposium on Bath Smelting. The Met. Society of AIME, Warrendale, PA; p. 353-375.

Maubon A. Recent developments of LWS operation and experiments in progress. In: Basic Oxygen Steelmaking – A New Technology Emerges. The Metals Society, London; p. 53-56.

Michaelis EM. 1979. Introductory address: A review of progress from Bessemer and Thomas to LD, LD-AC, OLP, Graef-Rotor, Kaldo, OBM/QBOP, and LWS. In: Basic Oxygen Steelmaking–A New Technology Emerges. The Metals Society, London; p.1-10.

Mousel R. LD-AC steelmaking at ARBED. In: Basic Oxygen Steelmaking – A New Technology Emerges. The Metals Society, London; p. 34-40.

Nakagawa R. Ueda T. Yoshimatsu S. Sato A. Mitsui T. Uehara I. Fukuzawa A.

Continuous Steelmaking in NRIM. In: Proceedings of International Conference on the Science and Technology of Iron and Steel. Tokyo, Sept. 7-11, 1970. Part I, p. 290-293. Patil BV. Chan AH. Choulet RJ. 1998. Refining of stainless steels. Chapter 12, In: The Making, Shaping, and Treating of Steel: Steelmaking and refining volume (Ed. Fruehan RJ). Pittsburgh, Pa. p. 715-718.

Ramacciotti A. Praitoni A. Spaggiari T. Imberti B. de Rosa G. Rotovert: A New Steelmaking process. In: Proceedings of International Conference on the Science and Technology of Iron and Steel. Tokyo, Sept. 7-11, 1970. Part I, p. 297-300. Rhydderch MJ. 1967. Spray Steelmaking, Journal of Iron and Steel Institute, p. 814-817.

Sandlöbes S. Senk D. Sancho L. Diaz A. 2011. In-situ measurement of CO- and CO₂concentrations in BOF Off-gas. Steel research int.82, 6. p. 632-637.

Savard G. Lee R. 1966. Improvements in Metallurgical Process, French Patent, No.1450718, 18 July 1966.

Srinivasan S. Ranganathan S. 1999. India's Legendary Wootz Steel. Bangalore: National Institute of Advanced Studies, and Indian Institute of Science.

Steinmetz E. Kuhn J. 1971. Kontinuierliche Stahlerzeugung. Klepzig Fachberichte,79, p.570-575.

Takahashi K. Tanabe H. Iwasaki K. Muroya M. Kikuchi I. Kawakami M. 1990. Key factors to improve post-combustion in pressurized converter type smelting reduction vessel; Tetsu-to-Hagané, vol. 76, No. 11, Nov. 1990, pp. 123-128.

Takashiba N. Nira M. Kojima S. Take H. Yoshikawa F. Development of the Post Combustion Technique in Combined Blowing Converter, Tetsu-to- Hagané, 75(1989), 89.

Tomàs E. 1999. The Catalan process for the direct production of malleable iron and its spread to Europe and the Americas. Institut d'Estudis Catalans, Barcelona,

Contributions to Science, 1(2): 225-232

Trenkler HA. 1953. The Metallurgical Principles of Steel Refining with pure Oxygen by the LD-Process. In: One Year LD-Steel. Vöest 1953. VUB, Innsbruck-Linz; p. 17-34.

Tylecote RF. 1984. History of metallurgy, 3rd impression, p. 182, The Metals Society, London

Umezawa T. 1992. Scrap Melting Process - Current Status and Future Prospects. Tetsuto-Hagane, ISIJ. 78, 4; p.12-18.

Wiborgh JG.1904. Järnets metallurgi. Föreläsningar. Albert Bonniers Förlag, Stockholm Worldsteel 2017. Steel statistical yearbooks. In: <u>https://www.worldsteel.org/steel-by-</u> topic/statistics/steel-statistical-yearbook-.html

Worner HK. Baker FH. 1971. WORCRA Steelmaking. In: Proceedings of International Conference on the Science and Technology of Iron and Steel. Tokyo, Sept. 7-11, 1970.

Part I, p. 277-282.

Zhang L. Oeters F. 1991. A model of post-combustion in iron-bath reactors, part 1:

theoretical basis. Part 2: results for combustion with oxygen. Steel Research, Vol. 62,

No. 3, p. 95-106-116.

Zimmermann R. Günther K.1975. In: Metallurgie und Werkstofftechnik, Band 2. VEB.

Deutscher Verlag für Grundstoffindustrie, Leipzig DDR. p. 197-200.