FUSED DOLOMA CONTAINING BRICKS FOR THE STAINLESS STEEL INDUSTRY

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1 INTRODUCTION

1.1 Modern Stainless converters - The AOD process

The AOD (Argon-Oxygen Decarburisation) process or variants of the AOD process based on the same principles (ASM, MRP, CLU etc.) account for >95% of the stainless steel made today – refer Table 1 below.

Tab. 1: Stainless production by process route

EAF - AOD	EAF – converter (AOD, MRP) - VOD	EAF - VOD	EAF – other converter (CLU, ASM)
76%	14%	4%	6%

In the AOD process an argon plus oxygen mixture is blown through tuyere pipes located in the lower sidewall of the converter - refer Figure 1 (below). The argon reduces the partial pressure of CO; this facilitates decarburisation to low levels in stainless steel which contains between 10 – 30% chromium. Most modern AODs are fitted with a supersonic LD type top lance which concurrently blows oxygen (down to 0.4% carbon) or oxygen plus argon (down to 0.1% carbon). Above 0.4% carbon, argon is not required for de-carburisation and blowing through the top lance dominates. During the first stage of decarburisation (above 0.4% C) the gas mixture through the tuyere is 70 – 90% oxygen with inert gas only required to cool the tuyere pipe. As decarburisation proceeds below 0.4% carbon the proportion of argon blown through the tuyeres is progressively increased with decreasing carbon content. Throughout decarburisation from 0.4%C to the end/ final carbon – the total gas flow tuyere rate remains constant. By the end of decarburisation the ratio of the gas mixture has reversed and comprises 70 – 90% argon. Most stainless steels contain nitrogen as part of the specification and this can be employed in place of argon during part of the process to reduce cost.

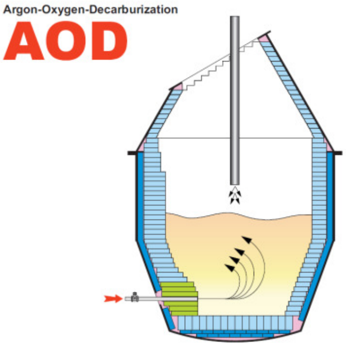

Fig. 1: Schematic representation of the AOD

During decarburisation significant quantities of chromium is unavoidably oxidized. Chromium oxide, plus smaller amounts of manganese oxide and iron oxide are recovered from the slag by adding ferrosilicon and / or aluminium – whilst stirring with argon to promote mixing and the slag-metal reaction. At this reduction (deoxidation) stage the slag is often highly basic (CaO + MgO / SiO_2 ≥1.9:1) and desulphurisation takes place at the same stage – a so called single slag practice. If the steel grade has an extra low sulphur specification then the first reduction slag can be removed and a second CaO rich slag added and stirred with argon. Throughout the entire process various metallic additions are made in order to control the temperature (typically between 1700 – 1740°C) and meet the final chemical specification of the steel being processed.

1.2 Refractory selection – Doloma the preferred choice

Since the vast majority of the world's stainless steel production has a very low carbon specification (<0.05%), this demands that a carbon free (preferentially) or very low carbon containing brick is used. The first AODs used magnesia-chrome working linings. These products ranged from 60% MgO direct bonded magnesia-chrome for use in the barrel to re-bonded fused grain 60% MgO in the tuyere pads. For the past 35 years however doloma has been the refractory of choice and is the working lining for over 90% of the world's AODs. Doloma is preferred over fired magnesia refractories because stainless steel refining uses highly basic lime rich slags – which in 90% of cases have been deoxidised (killed / reduced) using silicon. The solubility of MgO in silica based slags is high, 17% MgO in slags saturated with CaO rising to 30% in slags unsaturated with CaO. This strongly favours using fired doloma over fired magnesia based refractory.

When choosing between doloma and magnesia-chrome, doloma offers the following advantages:

- Slag chemistry – To obtain good refractory lifetimes with magnesia-chrome it is necessary to operate with a lower slag basicity (1.2:1 – 1.4:1 CaO/SiO_2 ratio) than would be desirable with doloma (>1.7:1). Operating with the lower slag basicity in most instances would necessitate a double slag practice for desulphurisation and steel cleanness. The recovery of reducible metal oxides (Cr_2O_3, MnO etc.) is also significantly worse with the lower basicity slag, however this would be partially offset by chrome pick up from the refractory.
- Spalling / thermal shock – although both brick types are susceptible to spalling, doloma is more plastic at high temperatures than magnesia-chrome so spalls significantly less when thermally cycled.
- Pre-heating – magnesia-chrome has to be pre-heated at a slower rate than doloma, otherwise micro cracks can appear in the brick. The minimum pre-heat time is 36-48 hours for magnesia-chrome, in comparison to 24 hours for doloma.

1.3 Typical Lifetimes and high wear areas of AOD linings

The lifetimes of medium - large AODs (30t – 180t in size) can typically range between 40 and 200 heats, depending on the operating conditions and product mix processed.

The highest wear areas on AODs are the tuyere pad followed by the slagline / trunnions. R&D effort is therefore focused on improving the performance of brick in these two areas.

2 RAW MATERIAL - SINTERED AND FUSED DOLOMA

Dolomite refractories contain calcium oxide and magnesium oxide, together with varying amounts of other calcium based compounds as impurities. All dolomite refractories are chemically basic. 'Doloma' is formed when dolomite is sintered at temperatures higher than 1700°C. Doloma refractory bricks may and are frequently enriched with magnesia to improve their volume stability at elevated temperatures – refer Figure 2 (overleaf). To further increase corrosion resistance larger crystal size fused magnesia may replace some of the sintered magnesia addition.

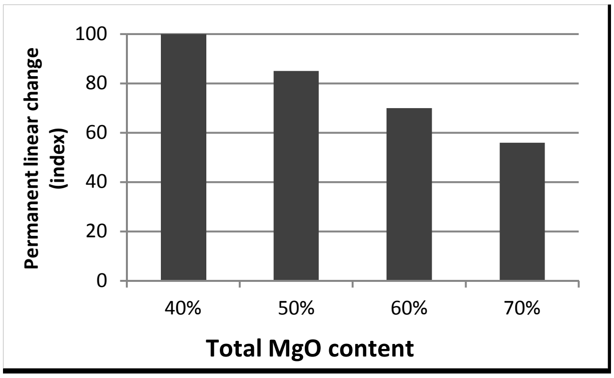

Fig. 2: Relative permanent linear change versus MgO content

The structure of doloma is periclase (MgO) crystals dispersed in a continuous matrix of lime (CaO). The impurities contained in the raw materials generate secondary phases consisting of calcium based compounds which typically have low melting points. At steelmaking temperatures this consequently leads to the formation of liquid phases at the hot face of the brick. In addition the residual open porosity in the doloma brick exposes the refractory to attack / penetration from CaO unsaturated silicates and aluminates present in the liquid bath. These are the mechanisms that result in the chemical corrosion of the lime matrix in doloma.

To improve the brick properties the total or part substitution of sintered doloma with fused doloma was investigated. A comparison of the properties of sintered doloma and fused doloma in Table 2 (opposite) shows, as expected, that fused doloma has a significantly higher density and lower porosity. Additionally the impurity level is reduced during solidification as it combines with CaO and is segregated out. As a consequence the CaO content in fused dolomite is lower and the MgO content higher compared to sintered doloma. The crystal size for MgO in the fused doloma (100µm) is of course significantly larger than is typically observed with sintered doloma (5-15µm). All the aforementioned features of fused doloma should result in enhanced resistance to slag penetration as well as improved volume stability at elevated temperatures.

Figure 3 (below) shows that the fused doloma has a distinctly different microstructure compared to sintered doloma. This will lead to the redistribution of secondary phases. The lower impurity content should result in being less sensitive to thermal shock.

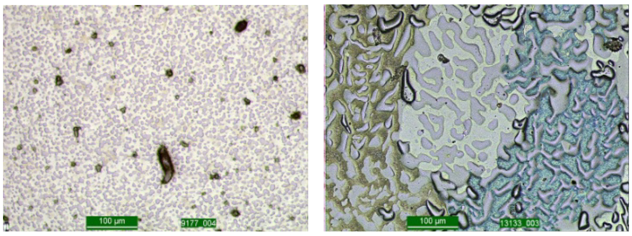

Fig. 3: Microstructure of sintered and fused doloma

Figure 4 (opposite) shows a block of fused doloma raw material for reference.

Fig. 4: Fused doloma block

Table 2 (below) gives an overview of the chemical composition and essential physical properties of sintered compared to fused doloma.

Tab. 2: Typical composition and properties of Sintered and Fused Doloma

Species	Unit	Sintered Doloma	Fused Doloma
Density	g/cm^3	3.20	3.38
Porosity	%	4.0	2.0
MgO	wt%	39.0	46.5
CaO	wt%	59.0	52.5
SiO_2	wt%	0.8	0.7
Al_2O_3	wt%	0.5	0.2
Fe_2O_3	wt%	0.6	0.1

3 FUSED DOLOMA FOR TUYERE ZONE BRICKS

3.1 High wear rates in the Tuyere Zone

The tuyere bricks are the bricks with the highest wear rates in any AOD lining, and the tuyere zone is a common failure area of stainless converters. The wear rates of the tuyere bricks typically range between 4 and 12 mm/heat mainly depending on the product mix and the operating conditions.

The following factors are the cause for the faster wear compared to other areas:-

- In AODs the metal flow is characterised by two elliptical currents – refer Figure 5 (below). The smaller left hand circular flow is directed against the tuyere wall resulting in refractory wear in the tuyere zone. The velocity of this smaller circulating current is higher than the larger right hand circular flow that is directed against the pouring side. The high velocity current leads to increased erosion.

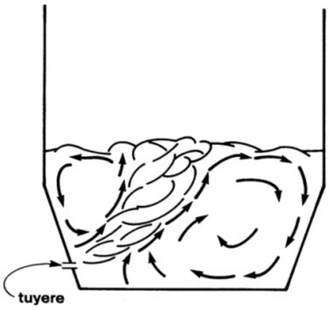

Fig. 5: Flow pattern in the AOD [1]

- Back attack - When the gas jet exits the tuyere pipe it rapidly expands on contact with liquid steel creating a gas plume. This momentarily pushes a pocket of liquid steel away from the tuyere pipe. This gas plume begins to rise and then quickly collapses under the weight of the steel bath, causing the liquid steel it had displaced to crash back against the refractory wall. The impact from this increases the refractory erosion above the tuyere pipes and is known as ‘back attack’.

- High temperatures – the reactions between the oxygen that exits the tuyere pipe and chromium cause local temperatures of ~2600°C in the steel bath which impacts on the hot face temperature of the tuyere brick.
- Thermal cycling – tuyeres consist of a copper inner tube and a stainless outer tube. Inert gas needs to be blown through the shroud when the converter is horizontal to keep the copper inner tube cool. This causes the tuyere brick to cool, which results in increased thermal cycling and hence spalling.

Because of the high wear rates the tuyere zone commonly dictates the performance of the overall lining. If this is the case, any performance increase in the tuyere zone will have a direct impact on the lining performance and the associated specific refractory cost.

3.2 Tuyere application

Internal trials were made using formulations with varying grain size distribution, fused doloma content and distribution. The formulation with the best overall test properties was selected for field trials. This contained over 50wt% fused dolomite blended with sintered magnesia and sintered doloma. The CaO content remained at 33%, the same as the standard formulation - refer Table 3 (below) – since when the CaO matrix in doloma is attacked by silicates it ultimately (eventually) leads to the formation of the high melting point phases C_3S and C_2S. It is therefore necessary to have a certain quantity of CaO present (available) in the formulation to restrict slag penetration.

The new formulation had a marginally higher MgO content, lower impurity content and increased density – all resulting from the substitution of sintered doloma with fused doloma. Although fused doloma is less reactive and creates less ceramic bonding during firing – a similar open porosity and cold crushing strength were observed on the final product. A significant advantage of the new fused containing formulation is its improved volume stability as illustrated by the refractoriness under load. The standard formulation shows a high temperature deformation below 1700°C, whereas no deformation is observed with the new formulation in this temperature range. Moreover the creep under load behaviour of fused doloma containing brick is significantly lower than the one of standard brick highlighting an expected lower deformation - refer Figure 6 (opposite).

Tab. 3: Typical composition and properties of the standard tuyere grade and the new fused doloma containing grade

Species	Unit	Standard Brick	Fused Doloma containing Brick
MgO	wt %	64.0	65.0
CaO	wt%	33.0	33.0
SiO_2	wt%	0.8	0.7
Al_2O_3	wt%	0.5	0.4
Fe_2O_3	wt%	0.5	0.7
Density	g/cm^3	2.98	3.00
Porosity	%	12.5	13.0
C.C.S.	MPa	70	70
M.O.R. 1500	MPa	2.4	3.0
R.U.L. $T_{0.5}$	°C	1650	>1700
C.U.L. 1500	%	3.0	1.0

3.3 Field Trial Results of Fused Doloma in the Tuyere Zone

To date the fused doloma containing tuyere grade has been tested in over 35 linings at several different customers with AOD sizes ranging from 50 to 180t, realising a reduction in wear rates of up to 16%. Refer Table 4 (opposite) for individual trial results.

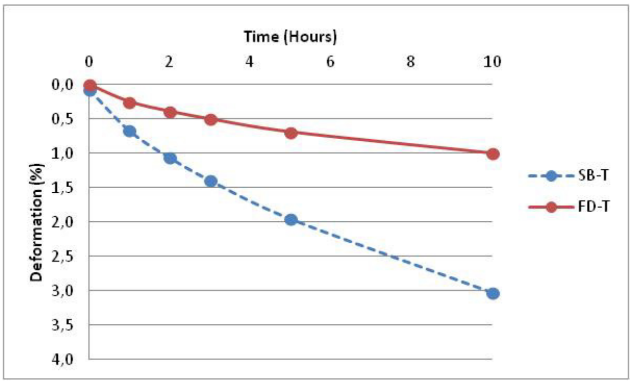

Fig 6: Creep under Load - tuyere; SB Standard brick, FD Fused doloma containing brick

Tab. 4: Field trial results of Fused Doloma containing Tuyere Zones

AOD size	No. of trial linings	Reduction in wear rates %	Tuyere failures	
			Standard tuyeres	Fused doloma containing tuyeres
50t	>12	N/A	23%	None
145t	3	-16%	None	None
75t	3	-5.0%	100%	100%
100t	4	-2.8%	68%	50%
82t	4	-8.9%	38%	None
180t	4	-5%	27%	None

Figures 7 and 8 (below) show the wrecking of used tuyere zones comparing a regular tuyere zone to a fused doloma containing tuyere zone. The photographs were taken from the exact same location in the tuyere zone and indicate the fused doloma tuyere zones have a more even wear compared to the standard tuyere zones.

Fig. 7: Wrecking of a standard tuyere zone

Fig. 8: Wrecking of a fused doloma containing tuyere zone (same AOD and location)

4 FUSED DOLOMA FOR SLAGLINE BRICKS

4.1 High wear rates in the Slagline

Compared to the tuyere zone the slagline is subject to less elevated temperatures and less thermal cycling. Nevertheless it is a high wear area due to the following factors:-

- Solid decarburisation slags cause abrasion in the slagline.
- Impact of alloying elements near the trunnion area

- Constant contact (in vertical and horizontal converter position) of the slag with the refractory in the so called ‘Slag Cross’

The slagline / trunnion / alloy impact area is therefore also a common failure area and a performance increase may lead to a reduction in overall specific refractory cost.

4.2 AOD Slagline application

A similar approach as described above for the tuyere grade was taken. Compared to the tuyere zone however the main wear mechanisms in the slagline are chemical corrosion, mechanical erosion and abrasion and there is less thermal cycling. Fused doloma grains are therefore used in the finer fraction of the grain size distribution. The selected formulation for field trials contains less than 50wt% of fused doloma grains. The properties compared to a standard slagline grade are shown in Table 5 (below). For the reasons previously stated the properties are marginally altered by the effect of fused doloma in the selected formulation whereas the high temperature volume stability is significantly improved – refer Figure 9 (below).

Tab. 5: Typical composition and properties of the standard slagline grade and the new fused doloma containing grade

Species	Unit	Standard Brick	Fused Doloma containing Brick
MgO	wt %	65.0	63.0
CaO	wt%	33.0	35.0
SiO_2	wt%	0.7	0.6
Al_2O_3	wt%	0.5	0.4
Fe_2O_3	wt%	0.6	0.5
Density	g/cm	3.00	3.02
Porosity	%	12.0	11.5
C.C.S.	MPa	70	70
M.O.R	MPa	3.0	2.5
R.U.L. $T_{0.5}$	°C	1650	>1700
C.U.L 1500	%	3.5	2.5

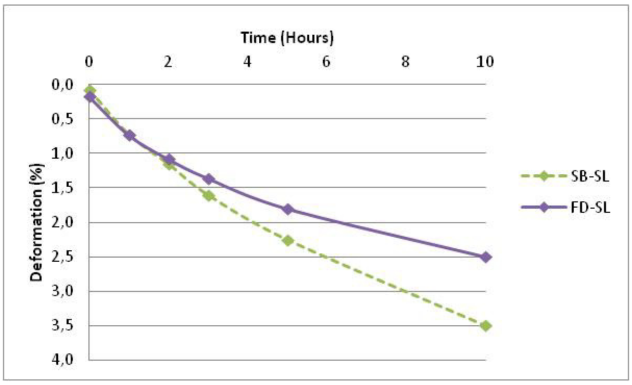

Fig 9: Creep under Load-Slag line; SB Standard brick, FD Fused doloma containing brick

As mainly an improved chemical corrosion resistance was expected due to an increase in crystal size of fused doloma, this tested formulation was selected for field trials.

4.3 Field Trial Results of Fused Doloma in the Slagline

The fused doloma containing slagline grade has been trialled in over 15 linings in AODs ranging from 50 to 180t at five different customers. The average wear rates were reduced by 3 - 19% compared to conventional magnesia doloma. Table 6 opposite shows the individual slagline trial results.

Tab. 6: Field trial results of fused doloma containing Slaglines

AOD size	Application	No. of trial linings	Reduction in wear rates
50t	Slagline	2	-3%
180t	Slagline	3	-7%
82t	Trunnions	5	-3%
99t	Slagline, Trunnions	7	-16%
145t	Slagline and tuyere side	3	-19%

5 CONCLUSIONS

- The tuyere zone and slagline are typically the two highest wear areas of AODs and other stainless converters.
- The wear rates in these areas dictate the overall lining performance. A performance increase in these areas will therefore increase the overall lining performance.
- The use of fused doloma containing tuyere zones increased the tuyere performance by up to 16% and significantly reduced the tuyere failures compared to standard tuyere zones.
- The use of fused doloma containing slaglines / trunnions increased the performance in these areas by up to 19% compared to standard slagline grades.
- The use of fused doloma tuyere zones helped to decrease the overall specific refractory cost of virtually all linings where it has been used. In the slagline an overall reduction in specific cost is only possible if its use is restricted to small areas, e. g. alloy impact panels.

6 REFERENCES

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