# CHROME-ALUMINA DVC LINING FOR STEEL DEPHOSPHORIZATION IN CORELESS INDUCTION FURNACES

Effect of phosphorus on mild steel

Phosphorus has actually various and negative effects on the final properties of steel. Basically it tends to increase the tensile strength due to the reinforcement of the ferrite solid solution. But a major adverse effect is the segregation of phosphorus – along with alloying elements like Mn or Cr – at the prior austenitic grain boundaries, forming phosphides that result in a strong alteration of resilience and ductility, also called embrittlement. Such characteristics significantly increase the tendency to cracking during cold work of steel and decrease the performance of steel reinforcement bars in concrete structures.
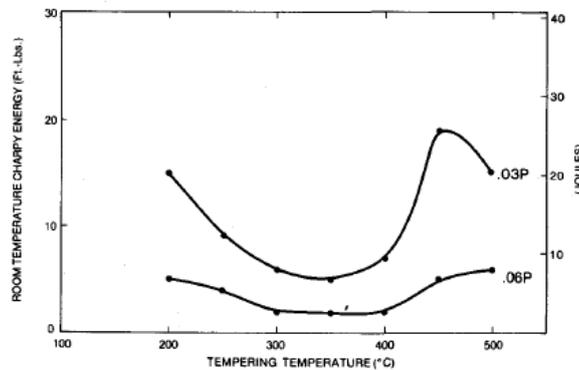

Fig.1: Impact of P content on steel resilience at room temperature [1].

The Indian standard for *High-strength deformed steel bars and wires for concrete reinforcement* (BIS 1786, amendment 1 from 2012 [2]) specifies that the phosphorus content in high-grade steel bars should remain below 0.04%.

Phosphorus removal

There is a strong interaction between iron and phosphorus and their redox characteristics are so similar that they usually get reduced simultaneously. This is why the phosphorus content is generally quite high in primary pig iron coming out the blast furnace or in sponge iron.

Fortunately it is yet possible to eliminate phosphorus by oxidation by using high basicity slags, in which the P_2O_5 activity remains low, even at very high concentration [3][4]. The partition coefficient of phosphorus between slag and metal can be much higher than 200 as soon as the basicity index (i.e. CaO/SiO_2) is higher than 2.
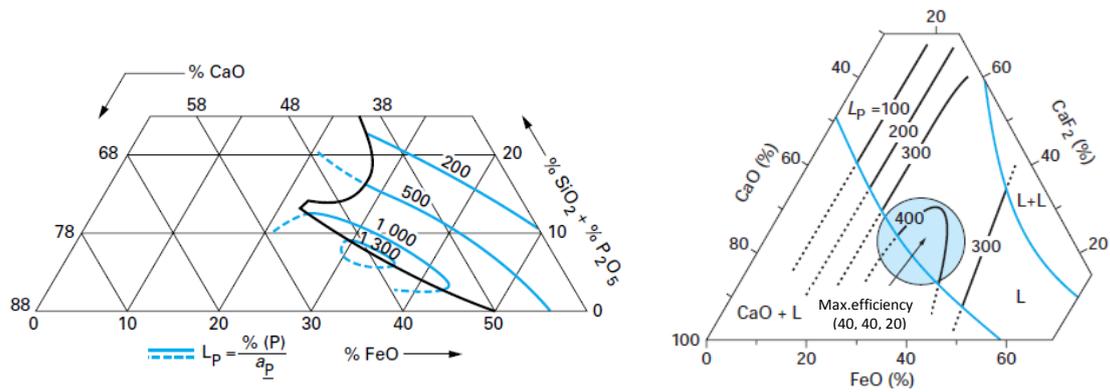
Fig.2: Partition coefficient of P as a function of slag compositions [5][6].

Typical slags use for dephosphorization (dephos for short) processes are usually based on lime and iron (II) oxide. Alternative slags based on barium can also be used. Moreover admixtures like soda or spath fluor are quite common.

Dephosphorization in coreless induction furnaces

Steel production through the induction furnace route represents about one third of the total steel manufacturing in India. The main advantages of coreless induction furnaces [3] lie in the their high versatility, the possibility to stop the furnace when necessary, the very good temperature control along the melting and treatment process, the capacity to melt any kind of alloy including low carbon steels…

The typical charge used to produce mild steel with an induction furnace is strongly dependent on the local availability of raw materials, but it usually consists in a mix of steel scraps, pig iron and DRI (directly reduced iron) in various proportions. This can result in variable amounts of phosphorus in the output steel, possibly up to 0.1%.

In spite of the above mentioned advantages, coreless furnaces present some drawbacks and limitations, especially with regard to potential dephosphorization process. First, the shape of the vessel is not fully adapted to any kind of slag treatment due to the small bath surface/volume ratio. However this can be balanced by the electromagnetic stirring of the melt, and also possibly by oxygen blowing and/or inert gas bubbling that are relatively easy to implement. Secondly the traditional refractory linings used in steel induction furnaces are not adapted to resist highly basic slags on the long term. Acidic linings based on crystalline silica cannot withstand contact with a dephosphorization slag, even for a short period. Oppositely, basic refractories based on magnesia are not adapted to the melting process when acidic slag is formed, and their sensitivity to thermal shock and moisture pickup make them poorly adapted to discontinuous processes.

The development of NRM (Neutral Ramming Masses) based on spinel-bonded alumina on this segment has truly made dephosphorization possible, while improving significantly the lining life under standard melting operation compared to alternative dry rammed materials [7]. The use of SAINT-GOBAIN NRM lining has already proven its cost-efficiency with regard to dephosphorization of DRI-based steel, compared to the use of low-phosphorus scraps. However the reduction of the NRM lining life consecutive to the additional corrosion rate linked to the dephosphorization slag has a strong economic impact for the steel manufacturer and is a serious impediment to the development of such process in coreless induction furnaces.

Alternative product to spinel-bonded Neutral Ramming Masses

Although NMR provide an interesting compromise in front of corrosion and thermal shock in steel induction furnaces, including possibly a dephosphorization process, they also exhibit some limitations related to their intrinsic design and microstructure. Their bonding system is based on *in situ* spinel formation at high temperature, which is known to provide good corrosion resistance. However the spinel formation comes with a significant volume expansion that tends to limit the mechanical strength of the sintered layer and does not really lead to small pores due to the sizing of the particles necessary to obtain a good ramming ability and a suitable shelf-life (reactivity of MgO fines). The development of the spinel ceramic bond is assumed to occur from 1200°C [7][8], but the various impurities coming essentially from the magnesia and the compressive stresses generated by the expansion of the hot sintered layer tend to provide a consolidation of the material in the back layers as soon as the temperature exceeds 900-1000°C.

Moreover, in spite of being a basic oxide, MgO is far from being inert in a typical dephosphorization slag. The solubility of MgO in a $CaO-FeO-CaF_2$ slag at 1550°C is about 4% but will quickly increase above 10% or more after progressive SiO_2 enrichment of the slag along the dephos process [7]. The table below displays an example of the evolution of a dephos slag in a lab coreless furnace lined with a basic 85% MgO lining. It is especially interesting to note the huge increase in MgO over time.

Exp. time	0	20 min	1 hour
CaO	63.6	59.6	31.8
Fe2O3	27.2	6.3	3.9
Al2O3	5.7	6.7	6.4
SiO2	2.3	16.0	16.8
MnO	< 0.1	3.9	9.9
Cr2O3	< 0.1	0.3	0.5
MgO	< 0.1	6.3	29.6

Table 1: Dephos slag evolution in over time (wt% oxides on calcined products).

Within this framework, the use of high-grade chrome-alumina dry refractories provides an interesting alternative to NRM based on spinel bonding. Chrome-alumina materials have been successfully used for decades in various steelmaking operations due to their high refractoriness and excellent corrosion resistance in various environments. Nevertheless their use as dry cements in coreless induction furnaces is not widespread. The use of MgO in combination with chrome oxide and alumina is still possible, leading to various spinel compounds, but should actually be minimized. SAINT-GOBAIN filed a patent application dealing with a new refractory solution, particularly adapted for dephosphorization in coreless induction furnaces and based on a chrome-alumina system. This material is defined as follows, in weight percentage of oxides relatively to the global material weight:
- more than 50% Al_2O_3, preferably more than 85%,
- more than 4% Cr_2O_3, preferably more than 7% and less than 15%,
- less than 20% MgO, preferably less than 1%,
- less than 5% CaO, preferably less than 0.5%,
- less than 3% SiO_2, preferably less than 0.5%,
- less than 5% Fe_2O_3, preferably less than 1%,,
- less than 30% ZrO_2, preferably less than 5%,
- less than 10% TiO_2, preferably less than 2%,
- the sum of $Al_2O_3+Cr_2O_3+Fe_2O_3+ZrO_2+TiO_2$ representing more than 80% of the material weight, preferably more than 97%.

The preferred solution is actually a new alumina-chrome Dry Vibrated Cement, which provides a unique solution to steel dephos in coreless furnaces, thanks to its optimized particle size distribution and ceramic bonding system.

## New Al-Cr DVC characteristics and benefits

The **new Al-Cr** bonding system is based on a chrome-alumina solid solution [9] that exhibits a very high resistance to ferrous alloys and slags. The slightly positive permanent expansion during sintering provides suitable densification without opening the pore structure or altering the hot face strength of the lining. The initial particle size distribution and the sintering mechanism lead to a microporous structure limiting any molten metal or slag penetration into the lining.

Characteristic after firing 1600°C	New Al-Cr DVC	Typical NRM
Bulk density	3.4	2.8
Open porosity (%)	15	25
Median pore size (µm)	< 1	6
Cold crushing strength (MPa)	85	20
Permanent linear change (%)	0.1	4

Table 2: Comparative properties after firing for New Al-Cr DVC and a typical spinel-bonded NRM used for steel coreless furnaces.

The selected raw materials and the nature of the ceramic bond lead to a high temperature sintering that minimizes sintered thickness and keeps most of the refractory lining in a non-sintered powder form, thus improving the resistance to cracking and the thermal insulation of the lining, in spite of the higher thermal conductivity of the sintered area. The figure 3 illustrates the comparative sintering behaviors of respectively **new Al-Cr DVC** and a typical spinel-bonded alumina NRM both exposed to a thermal gradient between 1600°C and ambient atmosphere. The ceramic bonding for the standard NRM is completed around 1360°C whereas the final sintering of the **new Al-Cr DVC** only occurs at 1450°C. And there is a similar 100°C difference on the primary consolidation as well.
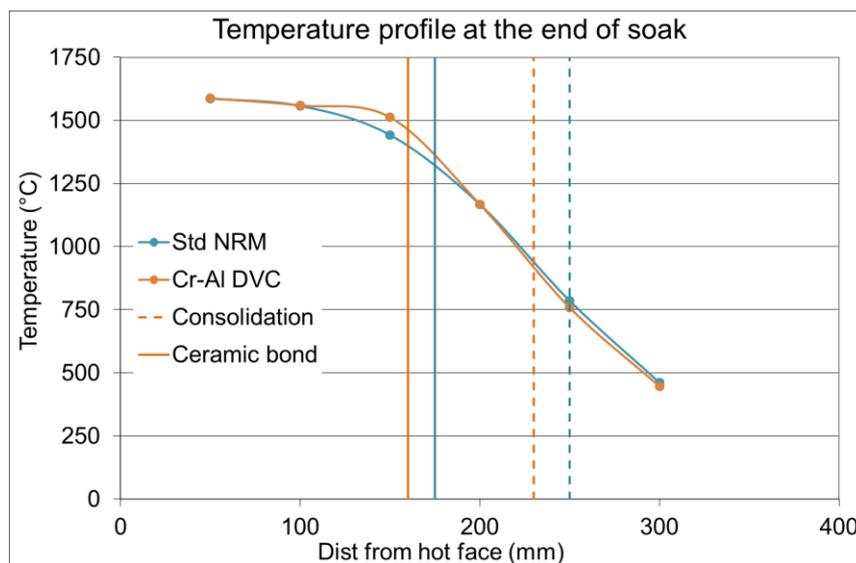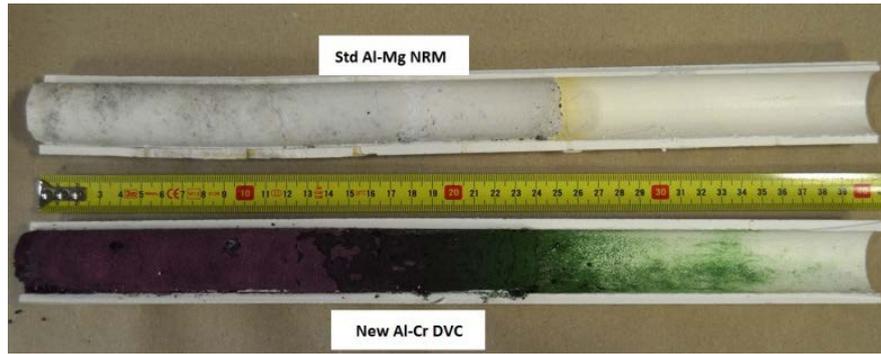
Fig.3: Sintering under thermal gradient of an Al-Cr DVC and a typical NRM.

The figure 4 shows an estimated comparison of thermal profiles through a steel coreless furnace lining in the cases of NRM and chrome-alumina. This illustrates the benefit of chrome-alumina that – in spite of a higher thermal conductivity – takes advantage of higher sintering temperature to decrease the global heat loss through the lining.
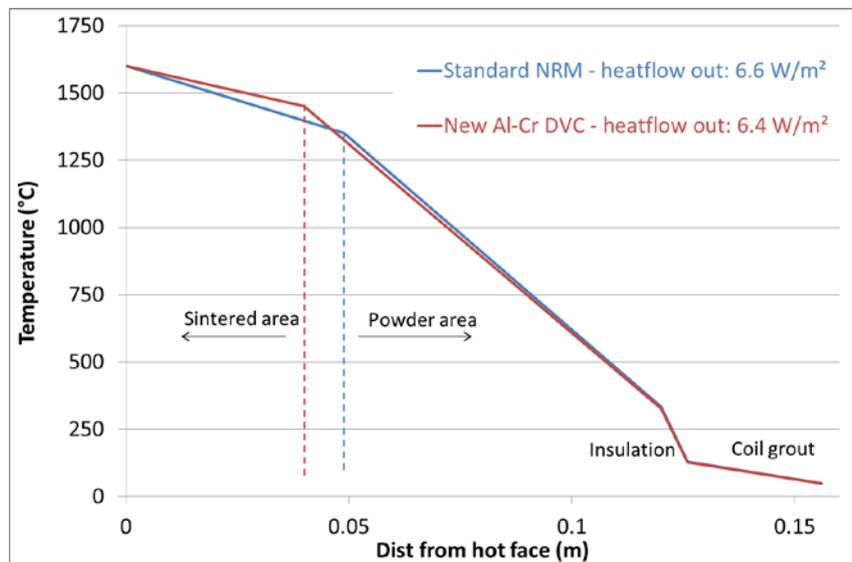
Fig.4: Thermal profiles through the lining for resp. NRM and New Al-Cr DVC.

As far as corrosion by dephos slag is concerned the benefit of the chrome-alumina system is quite obvious. Large cylindrical samples being 70 mm in diameter were immersed into a high-frequency coreless furnace containing 200 kg of Mn-steel reinforcement steel doped with 0.0.8% P and 10 kg of dephos slag having the composition given in table 3. The cylinder was then put in rotation at 30 rpm for 20 minutes. The temperature was kept between 1580°C and 1620°C during the whole test.

Slag component	wt%
CaO	58.8
Mill scale FeOx	30.3
CaF2	10.6

Table 3: Slag composition used for corrosion tests

The table 4 displays the results obtained on various refractory samples at the end of the tests. The superior performance of **New Al-Cr DVC** in these aggressive testing conditions is clearly visible in terms of both aspect and corrosion rate. The Cr_2O_3 content in the slag at the end of the test was close to 0.5%, which is similar to the concentration obtained without any contact with a chrome-containing refractory.

Material *Chemical analysis on calcined product*	New Al-Cr DVC	NMR	Basic ramming mass
	87.5% Al_2O_3 7.9% Cr_2O_3 0.4% MgO 3.0% TiO_2 0.6% SiO_2 0.2% CaO 0.1% Fe_2O_3 0.3% Na_2O	86.7% Al_2O_3 12.5% MgO 0.2% SiO_2 0.2% CaO 0.1% Fe_2O_3 0.3% Na_2O	83.9% MgO 13.9% Al_2O_3 0.9% SiO_2 0.9% CaO 0.2% Fe_2O_3 0.2% Na_2O
Sample aspect after testing			
Diameter decrease at slag line (%)	5%	29%	11%
Volume loss below slag surface (%)	4%	20%	35%

Table 4: Results of lab corrosion tests in dephos conditions.

Conclusions

SAINT-GOBAIN **new Al-Cr DVC** is the refractory solution to be used for dephosphorization in coreless induction furnaces. Its unique ceramic bonding provides excellent corrosion resistance to any slag, in particular highly aggressive basic slags encountered in dephos processes. The **new Al-Cr DVC** also exhibits higher sintering temperature, which helps to maintain a thick unsintered layer. Main positive consequences are a better resistance to crack propagation and finning, extended service life and to easier crucible extraction. The high mechanical strength and low permanent expansion of the **new Al-Cr DVC** after sintering leads to a dense hard hot face with superior abrasion and impact resistances, compared to alternative refractories like conventional NRM.

References

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