Fluxing options and slag operating window for Metso's DRI smelting furnace

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ABSTRACT

Decarbonization of the steel industry has recently attracted a lot of research and technological development. Most of the technological developments are centered around the replacement of blast furnace (BF), which has been the main primary smelting furnace in the iron making step of steel production. Replacement of the BF is not an easy task because of BF's many established capabilities over the years, especially its ability to use low grade iron feed.

In this regard, Metso has developed its own technology, Metso's Outotec DRI smelting furnace, to tackle this problem. The recently developed 6-in line electric furnace for DRI smelting can be used for primary smelting of DRI from blast furnace grade iron ore. Unlike the electric arc furnace, the DRI smelting furnace can handle larger slag volumes that emanate from the high gangue in BF grade DRI. Therefore, fluxing plays an important role in operating the DRI smelting furnace. This paper presents fluxing options and proposes slag quality and operating windows for the DRI smelting furnace. Also, the effect of slag on refractory durability will be discussed.

INTRODUCTION

Decarbonizing steel industry is one of the practical pathways to mitigate global warming. Carbon dioxide (CO_2) emissions from steel industry contribute a large share of greenhouse gases that leads to global warming. Carbon dioxide is responsible for about 73% of all greenhouse gases, while the balance is mostly from Methane (18%), N_2O (6%) and F-gases (2.5%) [Olivier et al, 2017]. Currently, and depending on geographical location, it is estimated that between 5 -14% of all CO_2 emissions come from the steel industry alone [Gielen, D., 20032; Kuramochi, T., 2016]. The Paris agreement puts an ambitious goal of limiting global temperature increase to 1.5 °C. And while this is a daunting task, it also presents process technology development opportunities.

Currently, blast furnace which is the dominant technology for iron making step of the steel production, is the main source of CO_2 emissions. This is because of the consumption of large amount of fossil reductants. For every ton of pig iron, there is ca. 0.5 tons of fossil reductants consumed [Fick eta al., 2014]. Opportunities for decarbonization of steel making therefore, depends on finding a low CO_2 emission alternative process to the blast furnace. This can be built around existing secondary smelting processes or completely stand-alone process.

Metso's alternative to the blast furnace, is a high capacity 6-in line DRI smelting furnace. When implemented together with a direct reduction process and current existing downstream processes, it is estimated to cut down CO_2 emissions by up to 60-80%, depending on electricity sources. Metso's DRI smelting furnace is based on Outotec proven proprietary technologies and should offer competitive advantages towards greener steel industry. It offers capacities of hot metal more than 1.2 million tons per year and can handle larger than electric arc furnace (EAF) slag volumes, making it possible to use DRI from blast furnace grade iron ores. Also, various types of direct reduced iron (DRI) from both natural gas and hydrogen based reducing processes can be used as feed.

DRI smelting furnace fluxing philosophy is built on using burnt dolomite and lime, in such proportion that regardless of the ore, the slag basicity stays within a narrow window. The fluxing philosophy also ensures that resultant slag can take impurities but stays within manageable viscosity.

Selection of suitable refractory is important, and Metso has conducted its own test work on various refractories on the market to determine the best candidate and operation mode for increased campaign life of furnace.

This paper presents data on fluxing philosophy and refractory selection for DRI smelting furnace. Operating window for resultant slag is assessed using thermodynamic software FactSage and the results are presented. Additionally, few observations made in ongoing refractory studies are discussed.

FEED FOR THE DRI SMELTING FURNACE AND FLUXING PHILOSOPHY

The design basis of the DRI smelting furnace is to target blast furnace grade iron ores, which have typically <67% iron in the concentrate and much higher gangue content of >5%. These types of ores are not suitable for smelting in EAF because of the low gangue tolerance of the EAF, and globally only about 3% of iron ores can be used to produce EAF grade DRI. Metso's ideal green steel flowsheet is by using hydrogen reduced DRI as in the Circored process, but the DRI smelting furnace can also handle DRI from shaft furnace and coal (Rotary kiln) based technologies. Tabel below shows typical feeds from the three DRI technologies. The numbers in the table are representative and not to be taken as standard for DRI available on the market today.

Table 1. Typical DRI specification from different technologies

	Natural gas reduced DRI	**Solid carbon reduced DRI**	**Hydrogen reduced DRI**
Total Fe (%)	>85	85 - 93	>85
Metallization degree (%)	90-94	88 - 90	85 - 92
Carbon content (%)	0.5 - 3	0.1 – 2	0
Gangue (%)	2.8 - 6	3 - 8	3-8

The metal product quality targets of the DRI smelting furnace include carbon of 2-3%, and low in phosphorus and sulfur. Depending on the target carbon content, the metal and slag temperature are typically 1500-1600 °C and 1600-1700 °C, respectively. The DRI smelting furnace uses burnt dolomite and lime as flux, with the proportions of these varying according to the composition of types of feed. The main determining components are the amount of CaO, MgO, Al_2O_3, and SiO_2 contained in feed. By comparison, typical blast furnace flux is limestone. The main components of the resultant slag are therefore the above 4 oxides. The basicity (CaO/SiO_2) is typically targeted somewhere between 1.2 -1.4 for most feeds. Additionally, it is important to keep the FeO content of slag at low levels (<5%) that enables it acceptable as raw material for the cement industry.

Thermodynamic calculations for assessment of operating window

The thermodynamic calculations in this study were carried out with FactSage 8.1. Thermodynamic parameters for the chemical system (Al_2O_3-CaO-FeO-MgO-SiO_2) were obtained from FactPS and FToxid databases. Impurities MnO, P_2O_5 and TiO_2 were left out of the calculated chemical system, because their contents are so small and not considered to be significant factors regarding the thermodynamic properties of the slag.

Liquidus temperature projections were calculated with FactSage for different compositions. Four projections with a base diagram of CaO-SiO_2-MgO were calculated with constant content of FeO (2.00%). Al_2O_3 content of the slag was 5.00, 10.00, 15.00 or 20.00% in different projections. Calculated temperature range for all the projections was from 1200 to 1800 °C (1473.15-2073.15 K). Interval between liquidus temperature isotherms was 20 °C. The final calculation was done with only those stable phases to make the final calculation faster and to produce smoother liquidus temperature isotherms.

Stable phases - solutions and compounds (pure substances PS) for the FactSage liquidus projections are listed in **Appendix A**.

Calculations with FactSage software package

The four liquidus projections calculated with FactSage are presented in Figures 1-4. At 5.00% Al_2O_3, the global liquidus temperature minimum of 1270-1280 °C is located near the four-phase intersection point [Clinopyroxene#1 / SiO_2_Tridymite(h)(s4) / Wollastonite] with the liquid slag. The composition of this four-phase intersection point at 1270 °C is 65.25% SiO_2, 28.10% CaO, and 6.65% MgO. At 10.00% Al_2O_3, the global liquidus temperature minimum of between 1192-1220 °C is located near the four-phase intersection point Clinopyroxene#1 / SiO_2_Tridymite(h)(s4) / Wollastonite with the liquid slag. The composition of this four-phase intersection point at 1192.7 °C is 68.46% SiO_2, 27.84% CaO, and 3.70% MgO. At 15.00% Al_2O_3, the global liquidus temperature minimum of between 1228-1240 °C is located near the four-phase intersection points [$CaAl_2Si_2O_8$_Anorthite(s2) / Cordierite / Orthopyroxene] and [$CaAl_2Si_2O_8$_Anorthite(s2) / Cordierite / SiO_2_Tridymite(h)(s4)] with the liquid slag. The composition of these four-phase intersection points at 1233.5 and 1227.8 °C are 70.33% SiO_2, 16.97% CaO, and 12.70% MgO and 73.45% SiO_2, 16.61% CaO, and 9.94% MgO, respectively. At 20.00% Al_2O_3, the global liquidus temperature minimum of between 1280-1300 °C is located near the four-phase intersection point [$CaAl_2Si_2O_8$_Anorthite(s2) / Melilite / Spinel#1] with the liquid slag. The composition of this four-phase intersection points at 1280 °C is 52.41% SiO_2, 37.70% CaO, and 9.89% MgO.

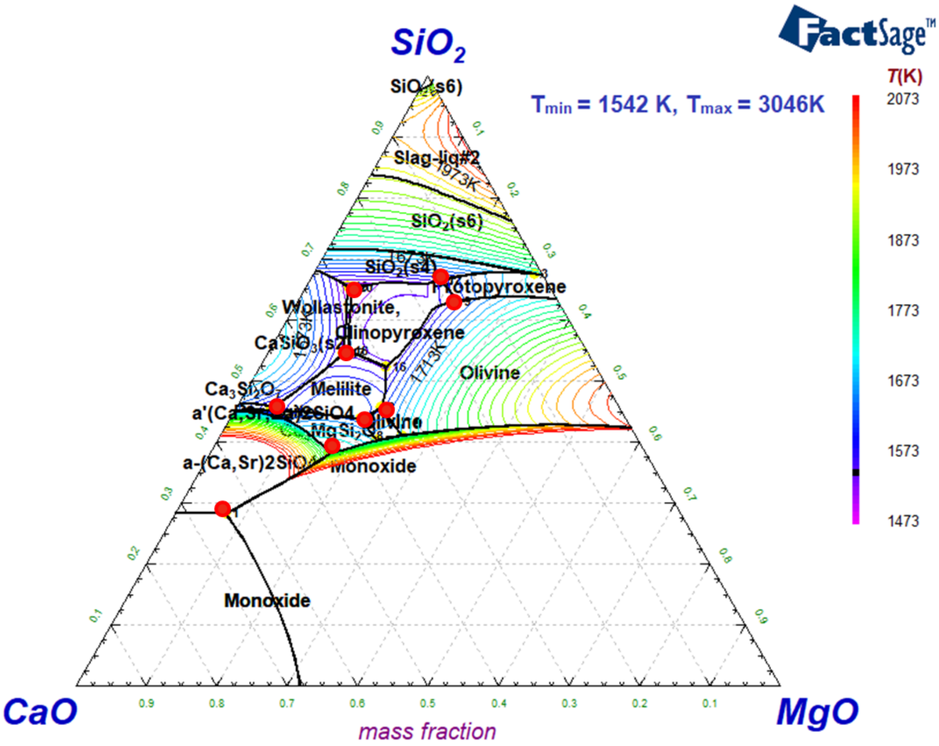


Figure 1. Liquidus projection in system $CaO-SiO_2-MgO$ with 2.00% FeO and 5.00% Al_2O_3 calculated with FactSage 8.1. The red dots indicate selected four-phase interaction points with the liquid slag.

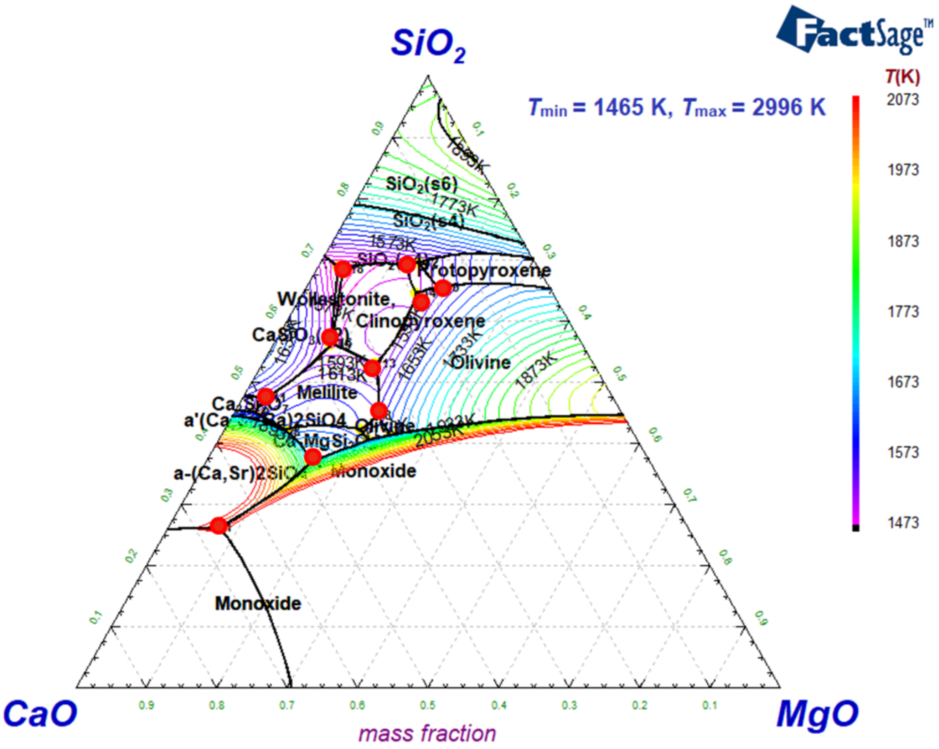


Figure 2. Liquidus projection in system CaO-SiO$_2$-MgO with 2.00% FeO and 10.00% Al_2O_3 calculated with FactSage 8.1. The red dots indicate selected four-phase interaction points with the liquid slag.

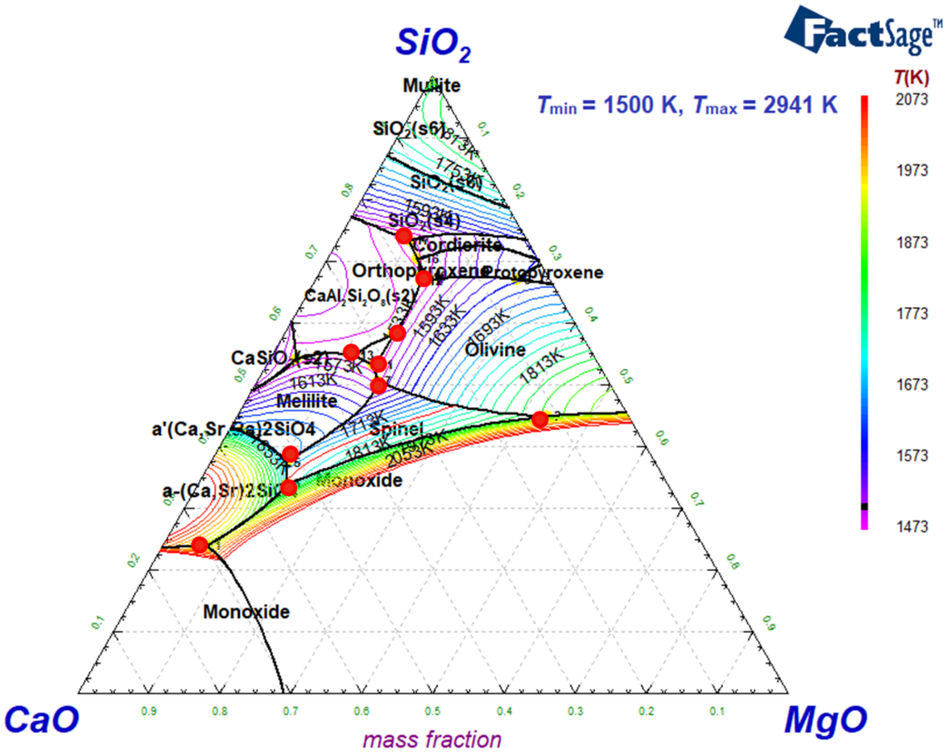


Figure 3. Liquidus projection in system CaO-SiO$_2$-MgO with 2.00% FeO and 15.00% Al_2O_3 calculated with FactSage 8.1. The red dots indicate selected four-phase interaction points with the liquid slag.

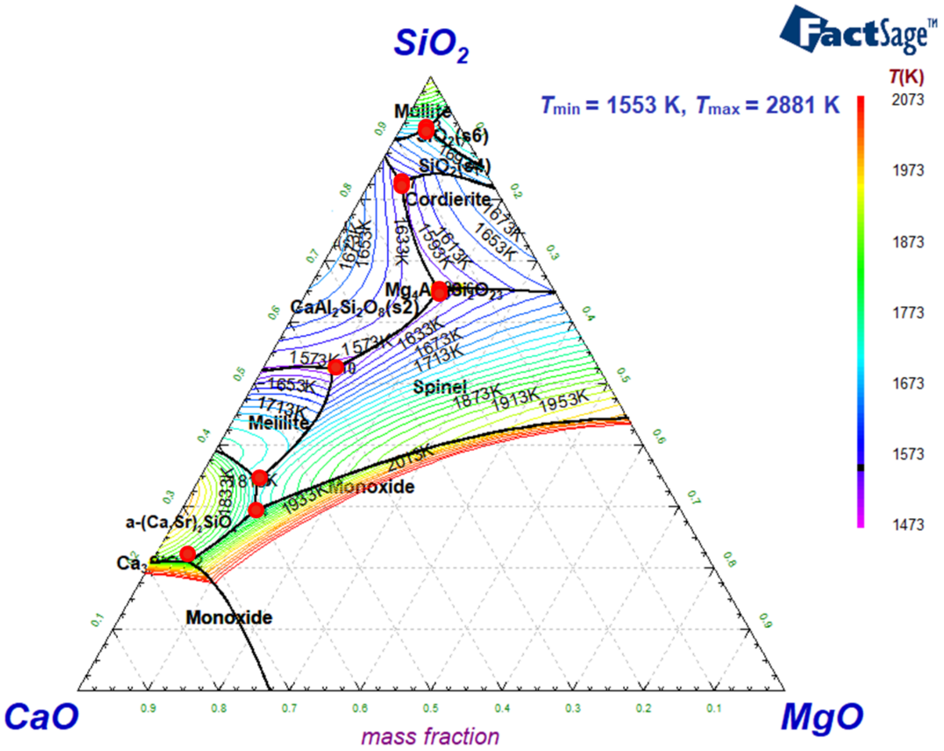
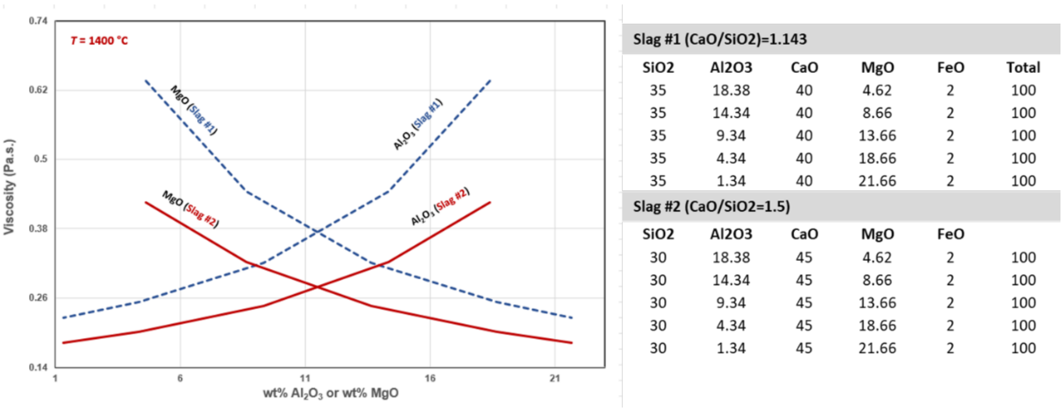


Figure 4. Liquidus projection in system CaO-SiO_2-MgO with 2.00% FeO and 20.00% Al_2O_3 calculated with FactSage 8.1. The red dots indicate selected four-phase interaction points with the liquid slag.

Viscosity calculations with FactSage

Viscosity values have been calculated for certain slag compositions. Slag #1 has a CaO/SiO_2 ratio of 1.143 and slag #2 has a CaO/SiO_2 ratio of 1.5. For both slags, only the amounts of Al_2O_3 and MgO were varied in a proportional amount.

The results obtained are illustrated in Figure 5. In general, at any given composition of Al_2O_3 or MgO, slag #1 with lower CaO/SiO_2 ratio (dashed lines in Figure 5) has higher viscosity than that of slag #2. In all cases, substitution of Al_2O_3 with MgO resulted in lower viscosity. For the calculated slag compositions (Figure 5), viscosity at 1400 °C remains below 0.65 Pa.s. Results are consistent with an earlier thermodynamic study conducted by Metso (internal report) [Pihlasalo et al., 2022].



Slag #1 (CaO/SiO2)=1.143					
SiO2	Al2O3	CaO	MgO	FeO	Total
35	18.38	40	4.62	2	100
35	14.34	40	8.66	2	100
35	9.34	40	13.66	2	100
35	4.34	40	18.66	2	100
35	1.34	40	21.66	2	100
Slag #2 (CaO/SiO2=1.5)					
SiO2	Al2O3	CaO	MgO	FeO	
30	18.38	45	4.62	2	100
30	14.34	45	8.66	2	100
30	9.34	45	13.66	2	100
30	4.34	45	18.66	2	100
30	1.34	45	21.66	2	100

Figure 5. Viscosities of two different slags (CaO/SiO_2=1.143 (dashed lines) and CaO/SiO_2=1.5 (solid lines)) with varying amounts of Al_2O_3 and MgO. Calculated with FactSage 8.1 software package.

Recommendation for DRI slag compositions at different operating temperatures

The operating temperature for the DRI smelting furnace is dependent on the liquidus temperature of the metal phase, which decreases as a function of carbon content of iron. Lowest liquidus temperature of Fe-C is 1147 °C at 4.3% C and melting temperature of pure Fe is 1538 °C. The metal temperature is required to be 50 °C higher than its liquidus temperature. The temperature difference between metal and slag is usually about 150 °C. This means that the slag temperature (=operating temperature) is required to be in the range of 1350 – 1750 °C. The slag needs 50 °C superheat, which then corresponds to slag liquidus of temperature range of 1300 – 1700 °C.

The suitable operating windows were found for operation temperatures between 1300 and 1500 °C. At 1600 °C, some operating windows were found but they are all high in MgO. At 1700 °C, no suitable operating windows were found, because inside those areas suitable based on liquidus temperature, the isotherms are close to each other, which makes operation difficult.

REFRACTORY TESTING

Refractories play a crucial role in smelting furnaces by containing molten slag and metal for long periods extending to several years usually referred to as a campaign life. They must withstand chemical attack, must be thermal resistant and must maintain a certain minimum mechanical strength during the campaign life. Choosing the correct refractory for a process is therefore mandatory.

Metso has been conducting its own test work to understand the best refractory for the DRI smelting furnace. Finger tests and crucible tests were carried out on two types of refractories. The choice of refractory was based on preliminary assessment of potential candidate refractories.

Finger test is performed by dipping a piece of refractory that has been cut into a finger like shape, in hot slag at temperatures resembling typical operating conditions. In this study, the slag was heated to 1500 °C and the samples were held in liquid slag for 6h while stirring during the test was helped by induction.

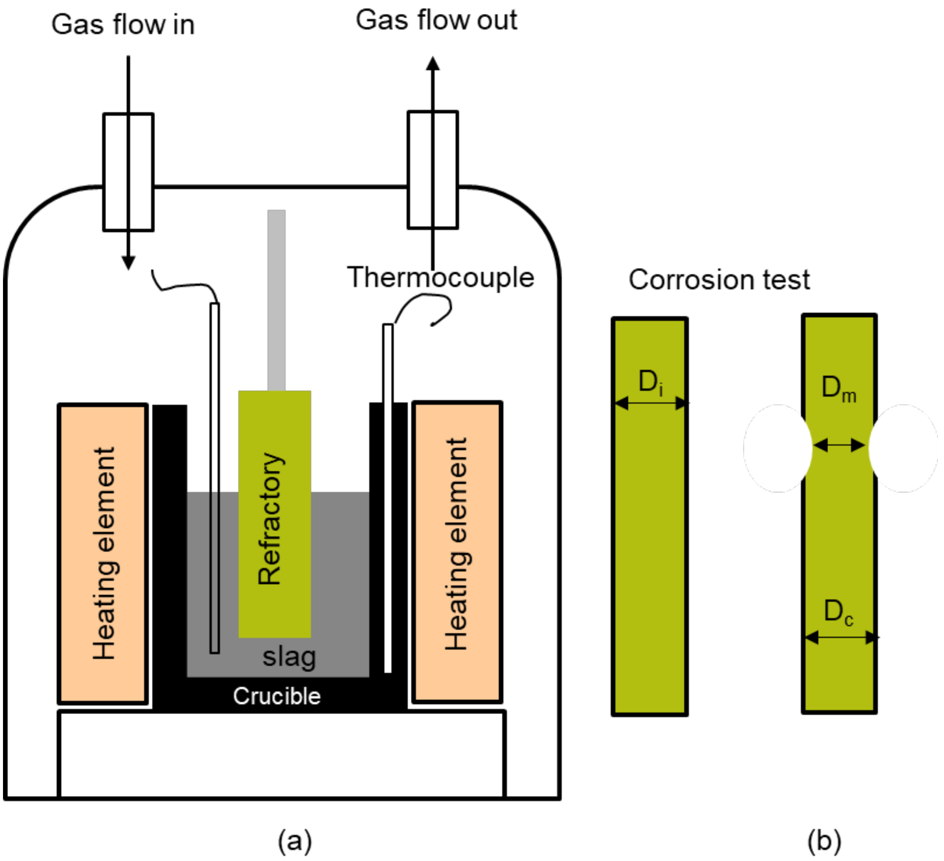


Figure 6. Typical experimental set up for finger tests; a) controlled inert atmosphere, sample evolution during tests in b), D_i is original dimensions of test sample, D_m, corrosion neck and D_c characteristic dimension of corroded piece in transverse direction sufficiently far off the corrosion neck, adapted from reference [Reynaert, C. et al, 2020]

Crucible test (or cup test) is done by placing molten slag a in a cup or crucible shaped refractory. Although similar temperature for slag as in the finger test is used, the holding time for this test is much longer. In this study, the slag was held at 1500 °C for about a week. Figure 7 shows the schematic of a crucible test set up. Table 2 shows the conditions for the finger and crucible tests. The refractories tested are magnesia-chromite and pure magnesia grades.

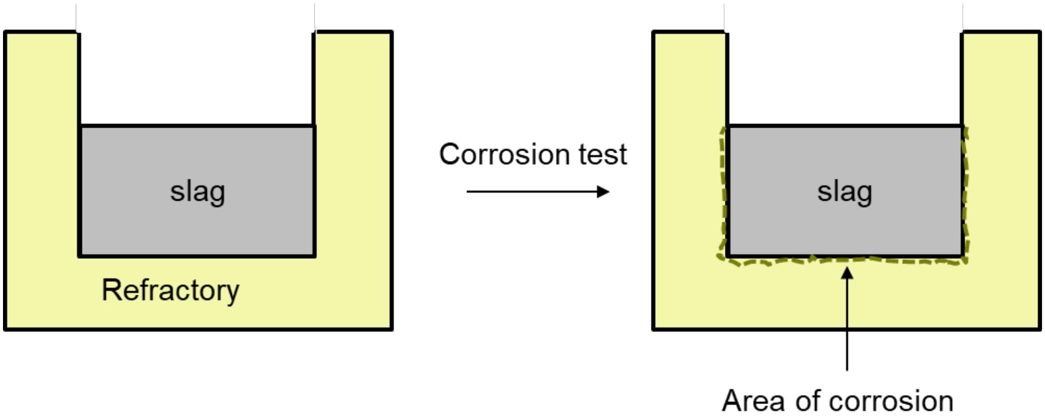


Figure 7. Schematic of crucible test showing slag infiltration area. Adapted from reference [Reynaert, C., et al, 2020]

Table 2. Test parameters for the refractory

Type of test	**Temperature (°C)**	**Holding time (hours)**
Finger	1500	6
Crucible	1500	168 hours

Results of finger tests are shown by the different forms of refractory degradation especially in the figures 8. Figure 9 shows after test crucibles used for cup test. Microstructures of refractory after tests (not included here) were evaluated using scanning electron microscope (SEM-EDS). Overall, the magnesia-chromite brick showed resistance to dissolution and cracking compared to the pure magnesia brick, which indicates that from the tested grades, magnesia-chromite is the recommended type of brick. In figure 8, there is more degradation in pure magnesia brick. The worst case is observed when using this type of refractory in slag of higher basicity, as shown in figure 8, the thin end of finger fell off during test.

However, this is an ongoing investigation, and more information will be generated to finetune the selection and to understand the various types of loads caused by the industrial operation.

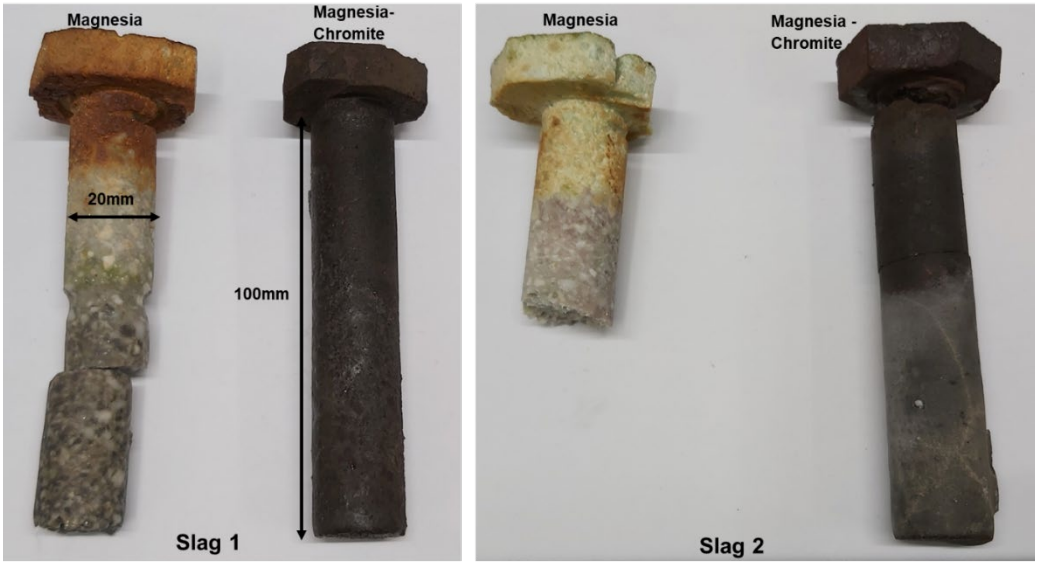
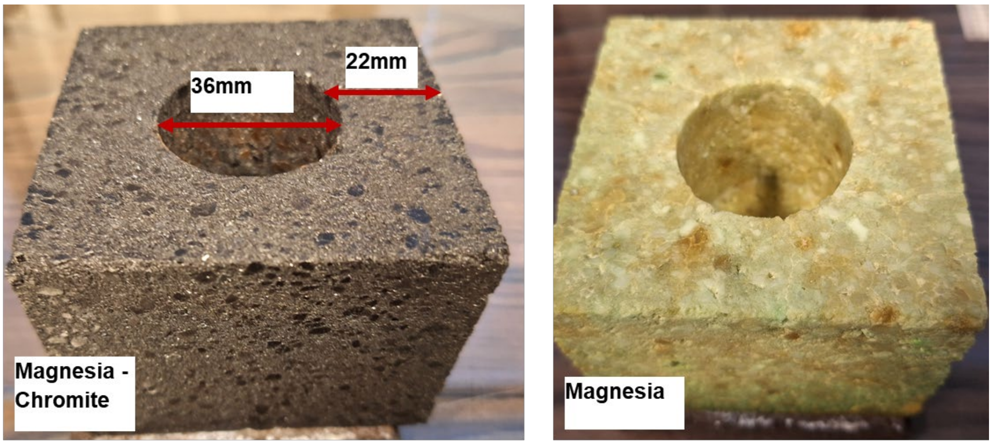


Figure 8. Results of finger tests for two selected refractory types. Slag of two different basicities 1.2 and 1.4 have been used and are labelled slag 1 and 2, respectively.



(b)

Figure 9. Samples of crucible tests showing drilled hole for slag containment

SUMMARY

Purpose of this paper was to present the fluxing philosophy of Metso's Outotec DRI smelting furnace. One of the main tasks was to identify operation window for smelting process, by using thermodynamic tools. The other purpose was to compare typical refractories for the DRI smelting furnace.

Suitable operation window in terms of liquidus temperature was found for production of iron metal with high carbon content. This operation window is large in terms of CaO/SiO_2 ratio, Al_2O_3 and MgO contents of the slag. However, operation area optimal in terms of liquidus temperature for iron metal with low carbon content is difficult to operate, because small changes in composition change operation temperature a lot. The slag obtained from Metso's DRI smelting furnace is of specification required for cement industry. For refractory selection, Magnesia chromite brick showed superior qualities for the DRI smelting furnace type of slag.

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APPENDIX A

Stable phases - solutions and compounds (pure substances PS) for the FactSage liquidus projections:

1 Slag-liq oxide [Al,Ca,Fe,Mg, (Mis.gap at high SiO2)]
2 Spinel (Cubic): Al- Fe-Mg-O or Al-Fe-Mg-O. Replaces AlSp.Mis. gap if Al,Fe(3).
3 Monoxide Rocksalt-structure: Fe(2),Ca,Mg; dilute Al,Fe(3). Miscibility gap if CaO is present.
4 Clinopyroxene: (Ca,Mg,Fe) [Mg,Fe,Fe3+,Al]{Al,Fe3+,Si}SiO6. Possible mis. gap when Ca is present.
5 Orthopyroxene: (Ca,Mg,Fe) [Mg,Fe,Fe3+,Al]{Al,Fe3+,Si}SiO6. Possible miscibility gap when Ca is present.
6 Protopyroxene: (Ca,Mg,Fe) [Mg,Fe,Fe3+,Al]{Al,Fe3+,Si}SiO6. Possible mis. gap when Ca is present.
7 Low-Clinopyroxene: {Ca,Mg}1{Mg}1(Si)2(O)6. Possible miscibility gap.
8 Wollastonite: CaSiO3, dilute MgSiO3, FeSiO3.
9 Bredigite: Ca3(Ca,Mg)4Mg(SiO4)4
10 a'(Ca)2SiO4: (alpha-prime (Ca)2SiO4); dilute Mg,Fe.
11 a-(Ca)2SiO4: (alpha-(Ca)2SiO4) - dilute Fe,Mg.
12 Melilite: (Ca)2 [Mg,Fe2+,Fe3+,Al]{Fe3+,Al,Si}2O7.
13 Olivine [Ca,Mg,Fe]1[Ca,Mg,Fe]1[Si]1[O]4. Possible mis. gap if Ca is present.
14 Cordierite: Al4(Mg,Fe)2Si5O18
15 Mullite: [Al,Fe]2[Al,Si,Fe][O]5, accounts for non-stoichiometry.
16 Ca2(Al,Fe)8SiO16: X-phase - (CaO)2[(Al,Fe)2O3]4SiO2
17 Ca(Al,Fe)12O19: CaAl12O19, dilute CaFe12O19
18 Ca(Al,Fe)6O10: T-phase (pure end-members are not stable)
19 Ca(Al,Fe)4O7: CaAl4O7, dilute CaFe4O7
20 Solution Phase Ca(Al,Fe)2O4. Possible miscibility gap (use [I] option).
21 Solution Phase Ca2(Al,Fe)2O5: Ca2Fe2O5, dilute Ca2Al2O5
22 Solution Phase Ca3(Al,Fe)2O6: Ca3Al2O6, dilute Ca3Fe2O6
23 Solution Phase M2O3(Corundum): Al2O3-Fe2O3 solid solution. Possible miscibility gap