OLIVINE AS SLAG CONDITIONER IN IRONMAKING, AND ITS EFFECT ON PROCESSING CHARACTERISTICS AND CO_2-EMISSION ERRO! A ORIGEM DA REFERÊNCIA NÃO FOI ENCONTRADA.

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Abstract

During 1980-85 many of the European iron producers replaced dolomite as slag conditioner with olivine due to the positive effects of olivine, especially in the sinter. Recently olivine has come in focus again due to its contribution to lower CO_2-emission in iron production. A numerical analysis study comparing the effect of olivine, dunite and dolomite as slag conditioner in the sinter and in the blast furnace has been made and verified with reported experimental results. The study indicates that the MgO supplying material preferably shall be used in the sinter. By replacing carbonate containing slag formers like dolomite, or acid slag formers like serpentine (dunite) with olivine, sinter quality, processing costs and CO_2-emission can be improved. The analyses have been carried out for iron ore with SiO_2 contents of 1, 3 and 6%, respectively. The use of olivine as MgO supplier to the sintermix is more favorable than dunite for all levels of SiO_2 and more favorable than raw dolomite if the iron ore contains 1-3% SiO_2. If the iron ore contains 6% SiO_2 the CO_2 emission will be slightly lower using dolomite compared to when using olivine.

OLIVINA COMO CONDICIONADOR DE ESCÓRIA NA FABRICAÇÃO DO FERRO E SEU EFEITO SOBRE AS CARACTERÍSTICAS DO PROCESSAMENTO E EMISSÕES DE CO_2

Resumo

Na década de 80, produtores europeus substituíram dolomita como condicionador de escória por olivina, devido aos seus efeitos positivos, especialmente no sínter,sendo comprado por vários estudos e trabalhos . Recentemente,olivina esteve em foco devido à sua contribuição para reduzir as emissões de CO_2 na atmosfera. Foram feitas análises numéricas comparando o efeito da olivina, dunita e dolomita como condicionadores de escória no sínter e nos altos fornos; os resultados foram verificados e comparados com resultados experimentais já apresentados. O estudo indica que MgO, deve ser utilizado de preferência na sinterização. Substituindo carbonato contendo formadores de escória - como dolomita bruta, ou formadores de escoria acida, como serpentina (dunita) por olivina, podem ser melhorados a qualidade de sínter, os custos de processamento e emissão de CO_2. Foram realizadas para minério com teor de 1,3 e 6% de SiO_2 respectivamente. Se o minério de ferro contém 1-3% SiO_2, a utilização de olivina como supridor de MgO para o sinter é mais favorável para todos os níveis de SiO_2 do que a dolomita bruta e a dunita. Se o minério de ferro contém 6% de SiO_2, as emissões de CO_2 serão ligeiramente menores se comparadas com o uso de dolomita e olivina.

Palavras-chave: Olivina; Dunita; Dolomita; Sinterização.

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1 INTRODUCTION

Olivine is a magnesium-iron silicate mineral without crystalline water. It has a basicity B3 = (CaO+MgO)/SiO_2 of 1.2 because of its high content of MgO, and is today one of the most commonly used slag conditioner in ironmaking in Western Europe.

Before 1975, dolomite was the common MgO-source in sinter and in direct charge to the blast furnace. But during the years 1975 -1985, dolomite was replaced with olivine by a major part of the iron manufacturers in Western Europe. The first use of olivine was as direct charge additive to the blast furnace with the aim to bind alkali and reduce the alkali recirculation in the blast furnace.(15) Reported effects were improved burden permeability, increased production and coke savings in the range of 3 to 5 percent. The positive effects on BF operation were reported,(6-10) to be caused by e.g. improved fluidity of slag when MgO is present which is positive for S refining and during tapping, the possibility to operate with lower CaO/SiO_2 and still achieve proper S refining and better K recovery to the slag, suitable softening and melting properties of agglomerates and a decreased Si content of hot metal.

The quality of sinter will have an indirect influence on the C consumption and CO_2 emission due to its effect on material losses, gas distribution and permeability in the BF. The quality of commercial sinters[11] produced from hematite iron ore agglomerates with serpentine as MgO supplying additive was shown to be superior to the one produced using dolomite considering strength measured as drum index and RDI < 3mm. Higher quality of sinter (produced from hematite ore) in terms of higher strength, lower disintegration after reduction and a higher reducibility was achieved with olivine compared to serpentine (dunite) in sinter plant trials carried out at TKS in an ECSC project.[12] During BF trials with both types it was clear that the pulverized coal (PC) injection rate could be increased and the BF permeability was improved with the improvement of these quality parameters of the sinter.

When raw dolomite was replaced by olivine as additive in sinter(1314) significant effects on the sinter production were stated in terms of 10-15% reduced coke consumption, 6-7% increased sinter output and approximately 5% increased sinter strength.. Main explanation for the favorable behavior of olivine compared to dolomite was the fact that olivine needed no calcination, while dolomite consumed 75% of the available sintering time for its calcination

Today olivine is used both as directly top-charged burden material and as an additive to iron ore sinter and pellets. The favorable effect on the coke consumption is an important contribution also with respect to CO_2-emission in the iron manufacturing process which has led to the study presented in this paper. The study is a comparison of three MgO containing primary slag formers; olivine, raw dolomite and serpentine and considering their effect on CO_2 emission and energy consumption during sintering and BF ironmaking

2 DESCRIPTION OF MATERIALS AND METHODS

The MgO supplying materials used in the estimation are olivine, raw dolomite and serpentine (dunite). The formula of olivine can generally be written as $(Mg, Fe)_2SiO_4$. Because of the chemical composition Mg_2SiO_4 with melting point of 1890 °C dominates over fayalite, Fe_2SiO_4 that melts at 1205 °C. Olivine has a low basicity B2, but B3 is 1.2 and the melting point is ~1800°C.

Table 1. Main chemical composition of MgO containing slag formers

	Fe	CaO	SiO_2	MgO	Al_2O_3	CO_2	H_2O *	B2**	B3***
Olivine	4.0	0.2	41.6	49.5	0.5	0.1	1.0	0,005	1.2
Raw dolomite	1.4	28.8	3.0	18.8	0.4	43.8	1.0	9.6	16
Serpentine	5.8	1.5	38.6	36.5	2.6	1.5	11.5	0.04	0.98

** Chemically bound water; ** B2 = w%CaO/w%*SiO_2*; *** B3 = (w%CaO + w%MgO)/w%*SiO_2

The main chemical compositions of MgO containing fluxes analyzed are stated in Table 1. As can be seen, the raw dolomite addition is related to quite high amounts of both CaO and MgO that is favorable for the use of it in iron ore agglomerates or in the BF. However, Mg and Ca but also other components of minor content are present as carbonates in the raw dolomite. During heating carbonates are decomposed according to the endothermic reaction (1) to e.g. CaO or MgO and CO_2. Calcinated lime or dolomite has high melting points close to 3000 °C.

$$MeCO_3 \leftrightarrows MeO + CO_2 \qquad (1)$$

Serpentine is a group of common rock-forming hydrous magnesium iron phyllosilicate ($(Mg, Fe)_3Si_2O_5(OH)_4$) minerals. It may contain considerable amounts of Al_2O_3 and some S. When serpentine is heated the content of chemically bond water is released in an endothermic reaction.

$$Mg_3Si_2O_5(OH)_4 \leftrightarrows Mg_2SiO_4 + MgSiO_3 + 2H_2O \qquad (2)$$

Table 2. Assumptions used in estimation of CO_2 emission and CO_2 produced from C needed for reactions related to the additives when heating the sintermix to 1350 °C.

MgO supplying material	Iron Ore SiO_2	Sinter basicity	CaO+MgO+SiO_2 in sinter
Olivine Raw dolomite Serpentine	1% 3% 6%	B2=1.7 B2=1.9 B2=2.1	16%

Thermodynamic estimations of the effect of slag formers on the energy consumption and CO_2 emission during sintering was made in HSC Chemistry[15] and combined with experimental trial data reported in the literature. Iron ore with three levels of SiO_2 content were chosen, 1%, 3% and 6%, respectively. The Fe content of these ores are 67%, 66% and 65%, respectively and the selection of iron ore compositions was based on an overview of iron ore available on the market.[16] The MgO supplying additives with composition stated in Table 1 were added to reach a MgO content of 1.6% and additional additives in terms of limestone and quartzite were assumed to be added to reach the desired basicity B2 of 1.7, 1.9 or 2.1 and a total content of CaO, MgO and SiO_2 that is comparable with that in industrial sinter produced in Europe(16-18) today.

Similarly, the numerical estimations are made for BF operation with compositions of pellets and sinters found in the literature(16-18) and stated in Table 3 were used in heat and mass balance calculations for the BF process. Restrictions made in the calculations were MgO content in the BF slag in the range 9-18.5%. High MgO content with stable and consistent operation has been stated and practiced in Swedish blast furnaces.[7] For the same type of operation the slag volumes can reach levels down to 145 kg/tHM and this was used as the lower restriction of slag volume. Except from MgO supplying slag former, quartzite and limestone was used to adjust the BF slag basicity for which the choice of B2 of levels 0.97 and 1.15 were considered in the estimations.

Table 3. Chemical composition of pellets and sinter used in estimations for the BF

	Olivine pellet	Acid pellet	Sinter 1	Sinter 2	Sinter 3	Sinter 4
Fe	66.8	66.9	60.6	56.8	59.6	59.7
CaO	0.45	0.55	7.1	10.6	7.8	8.5
MgO	1.6	0.52	2.30	1.49	1.91	0.44
SiO_2	1.9	2.5	3.3	5.3	5.1	4.3
Al_2O_3	0.32	0.25	0.58	1.1	1.2	1.2
B2	0.23	0.033	2.1	2.0	1.52	2.0

3 RESULTS

3.1 Estimation of Effect of Slag Formers on the Consumption of Reducing Agents and CO_2 Emission in Sintering

To reach the desired content of MgO the amount to be added is lowest when using olivine as shown in Table 4. When considering the additive and the limestone needed to compensate for the SiO_2 present in it the estimated CO_2 emissions are always lower when using olivine compared with when using serpentine. The CO_2 emission is also lower with olivine than with dolomite except when aiming a basicity B2 of 2.1. The CO_2 emission is 3-8 kg lower per tonne of sinter when olivine is used instead of serpentine.

Table 4. CO_2 emission caused by the MgO supplying additive and limestone added to compensate for SiO_2 contained in it

	MgO additive, kg/tonne	CO_2 kg/tonne sinter		
		B2=2.1	B2=1.9	B2=1.7
Olivine	32	22	20	18
Raw dolomite	83	21	21	20
Serpentine	43	29	26	23

Assume that a sintermix shall be made based on the values stated in Table 2. The CaO and SiO_2 content of the iron ore and of the MgO supplying additive as well as the desired basicity B2 will influence the amount of limestone that has to be added. E.g. using iron ore with 1% of SiO_2 an extra amount of SiO_2 and a corresponding amount of limestone has to be added to all assumed mixtures to reach the amount of slag normally present in the European sinter.(16-18) This is also the case for all basicities with mixtures of dolomite and B2=1.7 for olivine when the 3% SiO_2 containing iron ore is used. The energy consumption for heating the SiO_2 in the quartzite added is included in the estimations and also the heat and CO_2 released from the corresponding amount limestone added. Due this extra addition of quartzite to reach desired slag content of sinter the CO_2 emission is almost similar for 1% and

3% SiO_2 containing iron ore in the cases with olivine and raw dolomite, respectively. Addition of serpentine leads to a more significant increase in CO_2 emission due to its much higher SiO_2 content.

In Figure 1 the CO_2 emissions caused directly by the calcination of MgO supplying raw dolomite and limestone added to compensate for SiO_2 in olivine, serpentine and added quartzite is considered as well as CO_2 produced from C corresponding to the energy consumed in the heating of MgO supplying additive, quartzite and limestone. As can be seen in Figure 1, the use of olivine and raw dolomite is always more favorable than the use of serpentine and ~ 45-50 kg less CO_2 is released per tonne of sinter produced when using olivine compared to when using serpentine. The use of olivine is more favorable than the use of raw dolomite if the iron ore mixture contains 1% or 3% of SiO_2. The difference between olivine and dolomite increases with decreasing SiO_2 content of the iron ore and basicity of sinter. At a SiO_2 content of 6%, raw dolomite results in 1-6 kg lower CO_2 emission per tonne sinter compared with olivine. For iron ore with 1% SiO_2 or 3% SiO_2 olivine gives ~ 20-30 kg, lower CO_2 emission per tonne produced sinter compared with raw dolomite.

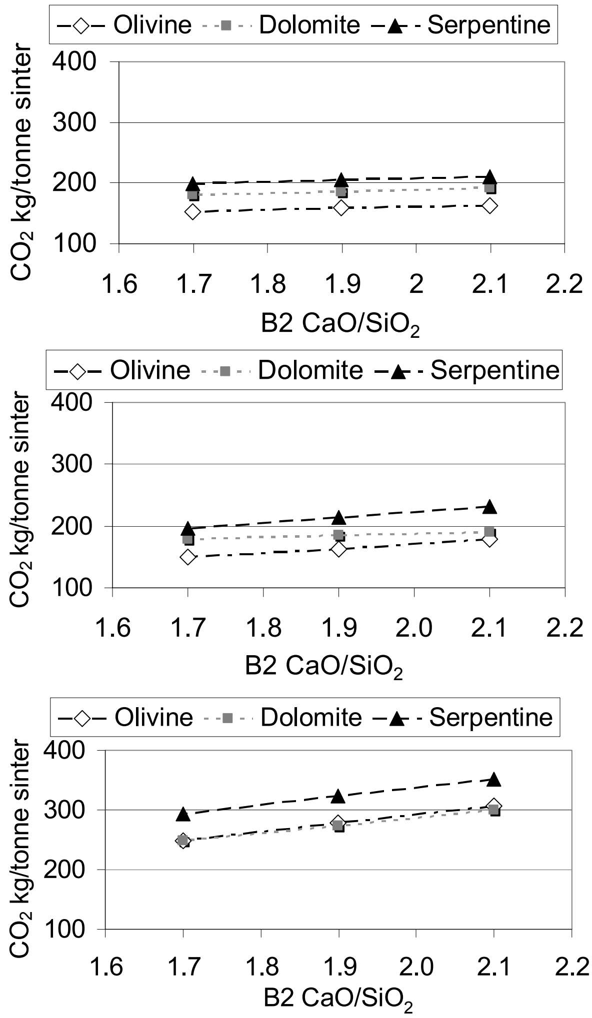

Figure 1. CO_2 emission caused by the addition of limestone, olivine, dolomite, and serpentine added to the sinter mix, from top to bottom with iron ore containing 1%, 3% and 6% SiO_2, respectively

3.2 Estimation of Effect of Slag Formers on the Consumption of Reducing Agents and CO_2 Emission in the Blast Furnace

In general it is more favorable to adjust the BF slag composition by adding low basicity pellets to the sinter compared with using additives as quartzite or olivine. By this the average Fe content of the ferrous burden is increased at the same time as the slag volume is minimized and its composition is adjusted. For each sinter type the estimated fuel consumption and CO_2 emission reaches minimum values for these conditions as can be seen from **Figure 2**. When using basic MgO containing sinter, acid pellets can be added and if the sinter contains less MgO than is desired for the MgO content of BF slag it can be mixed with MgO containing olivine pellets. There is also possible to design/choose sinter and pellets so that their softening and melting properties fits well and no additional slag formers have to be added to reach aimed BF slag composition. The addition of slag formers in terms of quartzite and olivine leads to slightly increased fuel consumption and significantly increased slag volumes as can be seen in Figure 3.

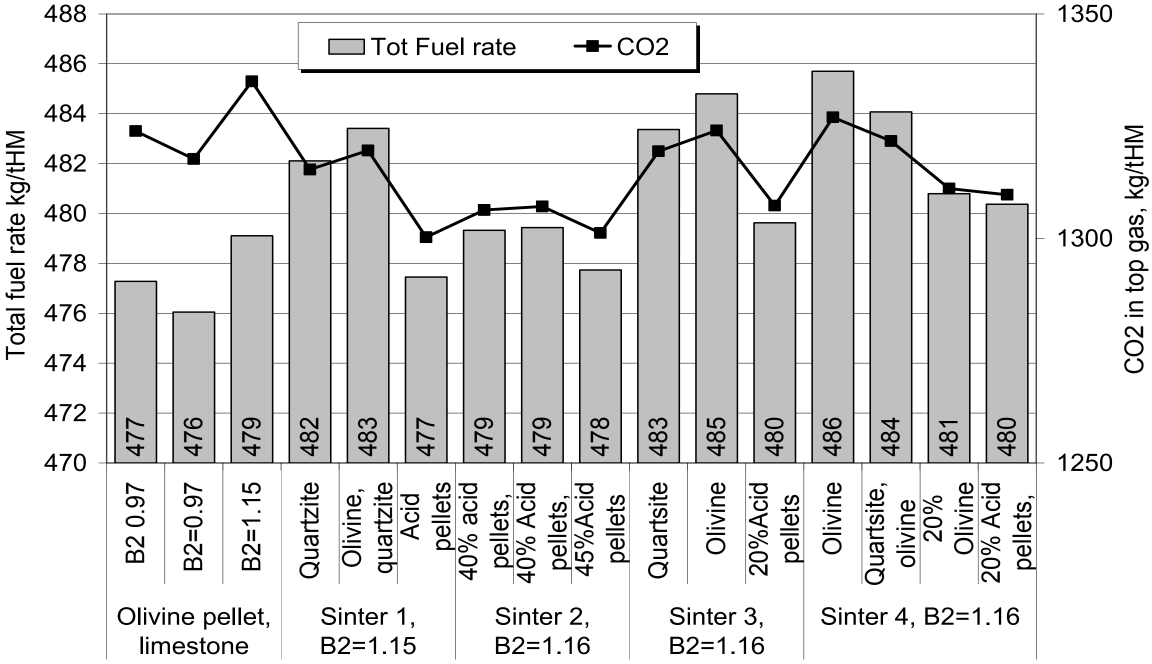

Figure 2 Fuel rate and CO_2 emission for varied burden, slag former additions and basicities of BF slag

The results indicates that the most positive effects on CO_2 emission in the BF is achieved by adding the slag formers in sinter mix instead of charging them directly into the BF. Compared to coke used in the BF, fuels of a lower grade can be used at the sinter plant. The lowest fuel consumption in the BF can be achieved by using olivine pellets with high Fe content, add limestone to adjust the basicity of the slag and minimize the slag volume. This combination is also quite favorable from CO_2 point of view. Sinter 1 and 2 combined with acid pellets as the main material for adjustment of slag composition is an even better alternative from the CO_2 emission point of view.

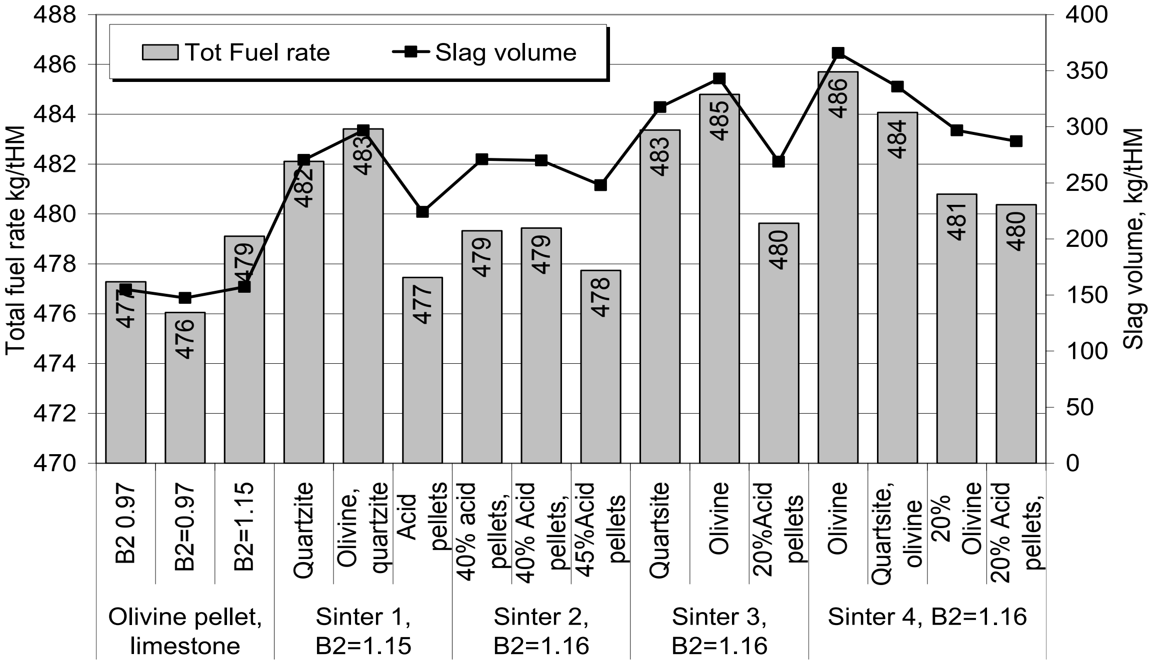

Figure 3 Fuel rate slag rate for varied burden and slag former additions and basicities B2=CaO/SiO_2 of BF slag

4 DISCUSSION

Results reported from industrial tests in sinter plants[13] indicate that the consumption of reducing agents can be expected to be influenced by the choice of MgO containing additive. In one trial when dolomite was replaced with olivine sand the coke breeze consumption decreased with 20.1% or from 59.2 kg/tonne sinter to 47.3 kg/tonne sinter. However, at the same time as the MgO content of sinter was decreased from 2.8 % to 1.7% and the basicity B2 from 1.63 to 1.42. Mass and thermal balance for olivine with the original sinter composition indicates that 4 kg of C or 4.5 kg of coke breeze (~89% C) more should have been needed if the composition of sinter had been kept constant. The estimated difference in coke breeze consumption rate, when changing over from raw dolomite to olivine is estimated to 7.4 kg coke breeze or 6.6 kg C and corresponds to 24 kg of CO_2. Similarly, dolomite was replaced by olivine in a sinter plant [14] and the energy consumption decreased with approximately 160 MJ/tonne sinter. This corresponds to 5.9 kg C or 6.6 kg of coke, which decreases the CO_2 emission with approximately 22 kg CO_2/tonne sinter produced. A total decrease of CO_2 emission with 21-25 kg/ produced tonne sinter can be expected based on the reported trials, which verifies the theoretical estimation of the iron ore with 3% SiO_2 showing a decrease of approximately 22 kg/tHM. The decrease of C consumption and CO_2 emission is estimated to be above 30 kg per tonne sinter when changing from raw dolomite to olivine using a 1% SiO_2 containing iron ore.

Results reported[11] from laboratory tests and for sinter pot tests with dolomite and serpentine used as MgO additive to the mixture show lower coke consumption when using serpentine compared to when using dolomite. The MgO content was 1.7% and the basicity B2 1.7 of the pot produced sinters. For the same sinter chemistry the difference in coke consumption is approximately 3 kg/tonne sinter which corresponds to 3.5 kg C or 12 kg of CO_2. However, to reach the same sinter chemistry with dolomite and serpentine iron ore with 0.72 % SiO_2 was used in case of serpentine and 3.7 % SiO_2 with raw dolomite. In the theoretical estimations iron ores with 1, 3 or

6% SiO_2 are used. Comparing e.g. serpentine addition to iron ore containing 3% SiO_2 with dolomite addition to iron ore containing 6% SiO_2 shows the same tendency as the sinter pot test results. With the same SiO_2 content of the iron ore raw dolomite will, compared to serpentine, result in significantly lower energy consumption and CO_2 emission according to heat and mass balance calculations.

Combined reported results indicate that the sinter quality in terms of RDI and disintegration changes with the additive used and the quality increases in the order dolomite, serpentine and olivine. The behavior of additives in the sintermix is dependent on the properties of the additive but also very much on the iron ore, other raw materials used in the mixture and process conditions during sintering. Improved sinter strength will contribute to decreased losses to the blast furnace dust, which decreases the C consumption and CO_2 emission. The sinter quality has as well shown to be of great importance for burden permeability and the possibility to decrease the coke rate and increase the PC rate.[12]

The addition of slag formers to European BF-s is in general low due to that sinter containing the slag former mainly is used as ferrous burden. The burden composition in terms of sinter, pellets and lump ore are designed to match and form a proper slag with minimum demand for additional adjustment. The amount of slag formers used by the majority of BF-s in Europe is e.g. less than 50 kg/tHM and the increased fuel consumption caused by top charging of carbonates is well known.[6] When the chemical compositions of industrial ferrous burden materials designed for a certain burden mixture are used in the numerical estimations it will be difficult to achieve good results with external slag formers added. The MgO supplying additives are often present in the sinter and pellets and additional amount added to the BF by top charging will therefore increase the slag volume and consumption of carbon in terms of coal and coke. With these low amounts of top charged slag formers it is problematic to achieve an even distribution in the ferrous burden and as a result the bosh slag composition may vary over the crossection area.

Positive effects in terms of absorbing alkalis has been shown for olivine [1] but these positive effects can be achieved when the olivine is present in the ferrous material as well.[8] As alkali recirculation is an energy consuming phenomena in the BF an improved alkali output to the slag will contribute to additional energy savings and further decreased CO_2 emission.

Limestone is used as additive in the sintermix and for adjustment of the BF slag chemistry. The CO_2 released due to the calcination reaction is about the same for limestone as for raw dolomite. $CaCO_3$ is calcinated at a higher temperature compared to $MgCO_3$ and the CO_2 release may react further with coke C in the solution loss reaction.

5 CONCLUSIONS

The energy consumption during calcination of high amount of limestone added to the sintermix and the variations of process conditions has a major impact on C consumption and CO_2 emission. The type of MgO containing slag former added e.g. olivine, serpentine or raw dolomite has impact on the energy consumption and CO_2 emission as well.

The chemical compositions of the iron ore concentrates used have influence on the choice of MgO supplying additive for minimum fuel rate and CO_2 emission. If the iron ore concentrate contains considerable amounts of SiO_2 and has quite low Fe content an additive with low SiO_2 content can be used to keep the Fe content high and limit the gangue content of the produced agglomerate. If the iron ore concentrate contains lower amounts of SiO_2 and has high Fe content olivine is a suitable slag former.

Theoretical estimations show lower energy consumption and CO_2 emission when using olivine compared to serpentine for iron ore with 1%, 3% or 6% SiO_2. Olivine is more favorable than dolomite if the iron ore contains 1-3% SiO_2. If the iron ore contains 6% SiO_2 the CO_2 emission will be slightly lower when using dolomite compared to when using olivine. Similar effects of the type of MgO containing material on the energy consumption have been shown at industrial scale when changing from dolomite to olivine as MgO supplying material added to the sintermix.

In general it is more favorable both from process point of view and for the total fuel rate and CO_2 emission to add MgO supplying slag formers to the sinter mix before sintering and charge these agglomerates into the BF compared to charging slag formers directly into the BF. By mixing pellets with high Fe content with sinter the Fe content of the ferrous burden is increased and the slag volume minimized and positive effects are found on the fuel consumption and CO_2 emission.

To reach low consumption of reducing agents and CO_2 emission in the BF under stable operation the charging of olivine pellets with high iron content and low gangue content allowing minimum slag volume is a highly favorable alternative. Another alternative is operation with sinter of high Fe content produced from low SiO_2 iron ore with olivine as MgO supplying additive.

REFERENCES

1 CURRIER, J.W, The function of olivine in the blast furnace applications, Ironmaking Conf. Proc., Vol. 47, Toronto, Ontario, Canada, 1988, pp 387-397
2 CURRIER, J.W; EHLERT, T.C, New perspectives on the behaviour of alkalis under blast furnace conditions, Proc. Ironmaking Conference, Vol. 47, Toronto, Ontario, Canada, 1988, pp 579-588
3 ERICSON,B-O; WIKSTRÖM, J-O, AHNQVIST, A, Blast furnace operation with 100% pellet burden in SSAB´s no.2 BF at Luleå works, Scand J. Metall., 13, (5), 1984, pp 316-318
4 SCHEEL, J.H, Blast furnace alkali control practice at Armco, Proc. Ironmaking Conference, Vol. 40, Toronto, Ontario, Canada, 1981, pp 278-285
5 Olivine and dunite – blast furnace usage adds new dimension, Industrial Minerals, May 1977, pp 39-49
6 BISWAS, A. K., Principles of Blast Furnace Ironmaking, 1981
7 HALLIN, M., THULIN, D., TOTTIE M., LKAB-pellets in the BF, Ironmaking conf. proc., pp 287-291 (1994)
8 ELIASSON E., HOOEY, P. L, ANNERSTEN, H., LINDBLOM B., Formation of Potassium slag in Olivine fluxed blast furnace pellets, Ironmaking and Steelmaking, Vol. 34, No. 5 (2007)
9 The Iron and Steel Institute of Japan, Blast Furnace Phenomena and Modelling, (1982)
10 WIKSTRÖM, J-O., DE BRUIN, T., The use of olivine in ironmaking, Mefos report (1995).
11 HSIEH, L-H., WHITEMAN, J.A., Effect of Raw Material Composition on the Mineral Phases in Lime-Fluxed Iron Ore Sinter, ISIJ Int., Vol 33 (1993), No. 4, pp 462-473

12 Fe-burden quality at high coal injection rates, EUR 20106EN, ECSC steel publications (2002)
13 WYOSOCKI, H., PÜCKOFF, U., FADGYAS, J., KISTER, H., Verbesserung von Sinter qualität, Leistung und Energieaufwand bei Sinteranlagen ohne Erzmisch betten der Hoechst Hüttehwerke AG, Dortmund, Stahl und Eisen (1983), No. 14, pp 703-708
14 ZIMMERMANN, K-A., PETERS K-H., BEER H., Mischbett und Sintertechnik bei der Möllervorbereitung im Werk Schwelgern der Thyssen AG, Stahl und Eisen 103 (1983) No. 14
15 ROINE. A, HSC Chemistry, Outokumpu Research OY, Pori Finland, ISBN 952-9507-05-04, www.outokumpu.com/hsc
16 Iron & Steel Works of the World Directory 2007", 17th Edition, Metal Bulletin, Dec. 2006
17 KORTMANN. H. A., LUNGEN H. B., RITZ. V. J., Quality Requirements of Burden Materials and Testing Methods used in Germany, Ironmaking Conf. Proc. 1992
18 HOOEY, P.L., Reduction and high temperature behaviour of iron ore sinter made from magnetite fines, dissertation University of Oulu, (May 1999)