Dolomite as a flux for High-Alumina Blast Furnace Slags

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B LAST FURNACE operators at Jamshedpur have to face a peculiar problem arising out of the high concentration of alumina in the slag. The normal analyses are $37\cdot3-37\cdot8\%$ CaO, $3\cdot4-3\cdot9\%$ MgO, $30\cdot4-31\cdot5\%$ SiO₂, $26\cdot2-27\cdot0\%$ Al₂O₃, $0\cdot69-0\cdot78\%$ FeO and $0\cdot69-0\cdot82\%$ S. The actual level, i.e. 26 to 28% is much higher than that common elsewhere and brings into force a series of adverse effects. Briefly, these consist of the greater viscosity of the alumina slags, greater tendency towards silicon reduction, and less efficient desulphurisation. As a result, it becomes rather difficult consistently to produce low-sulphur hot metal without exceeding the silicon level normally specified for basic iron.

In order to overcome the principal difficulties introduced by the high alumina contents two possible remedies suggest themselves : the first is the dilution of alumina to lower concentrations by additions of extra slag-forming materials, and the second involves the use of a suitable flux to counter the specific effects of alumina. Of these, the first method cannot be recommended because it would involve extra flux, extra coke and lower production rates and thus increase the cost of metal considerably. It is therefore used in local practice more as an occasional remedy; silicious banded-haematite-quartzite is introduced in the ore burden for this purpose. The second alternative is, therefore, more attractive, and dolomite is the obvious choice for the flux since the physical effects of increased magnesia contents are just the opposite to those of alumina. Hence, a series of extensive trials were carried out to ascertain the specific influence of incorporating various proportions of dolomite in the burden. The results of these campaigns are discussed here with specific reference to use of dolomite for high-alumina slag operation.

Origin of high alumina contents

Since the occurrence of such high proportions of alumina is rather uncommon, it is pertinent to discuss the main sources of alumina as found in local practice. For a typical burden¹ used for the production of 1.25% Si iron, one can compute the contributions made by various raw materials, as follows :

	Contribution %			Total input,
	Ore	Coke	Limestone	lb/ton of metal.
Al ₂ O ₃	60.6	36.0	3-1	325
SiÕ,	45.6	45.0	7.7	417
CaŐ		4.2	95.8	380

It is thus seen that the ore mix represents the major source of alumina and the influx of high ash from



FIG. 1 - EFFECT OF ALUMINA/SILICA RATIO IN THE ORE MIX ON SLAG ANALYSIS.

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¹ L. N. Collins-Tisco, 2 (1955) pp. 108-119.

the coke serves to decrease the final concentration of alumina in the slag. That the ore mix is in fact the major source is further emphasized by the correlations in Fig. 1, which shows that the steady rise in the alumina content of blast furnace slags at Jamshedpur over a period of 25 years² is clearly the result of the increased alumina/silica ratio in the ore mix. The high values of the correlation coefficients of the two regression lines drawn in the diagram prove that the relationships are quite significant.

Effects of high-alumina contents

The principal effects of high-alumina contents have been enumerated at the outset and it now remains to dilate on only those directly concerned in the evaluation of the results of the dolomite trials, namely, the control over silicon and sulphur contents of the metal. Other aspects of high-alumina slag operation are described fully in recent papers^{3, 4} to which a reference may be made.

The tendency to produce higher silicon metal with increasing concentration of alumina in the slag may be explained on the basis of results of equilibration experiments of Chipman and co-workers⁵. For example, as seen from Fig. 2, an increase in the alumina content from 10 to 20% causes a rise in the equilibrium concentration of silicon from about 13% to 16%. That these results of laboratory experiments are substantiated by operation data, where equilibrium is not attained, is vindicated by Fig. 3 based on local practice. It is clear from this diagram that the average silicon content has gradually risen over the recent years as a result of the rise in the alumina content of the slag. It should be mentioned here that the basicity ratio has not been altered significantly during this period and hence the observed effects can be attributed directly to the alumina contents of the slags. A better appreciation of the problem is had by examining not only the average silicon content, as in Fig. 3, but the percentage distribution of casts according to their silicon contents shown in Fig. 4. Here any particular point represents the frequency of occurrence of casts in the appropriate ranges of silicon from all the casts made in each month. Though there is a considerable scatter in the points, arising from the effects of numerous operational variables, the overall influence of alumina content is distinctly evident. It is seen that an increase in alumina content lowers the frequency of casts containing up to 1.30% Si and also up to 1.40% Si; on the other hand it increases the tendency for higher silicon contents in the metal.

- ² Unpublished work by the Statistical Dept., T.I.S.Co., on "Statistical evaluation of the effect of changes in the composition of blast-furnace raw materials on pig iron quality and furnace operation during the period 1939-1955".
- ³ H. Schrader—Trans. Ind. Inst. Metals, 4 (1950) pp. 25-63.
 ⁴ H. Schrader and P. Mehta—Tisco 2 (1955) pp. 193-196.
 ⁵ J. C. Fulton, N. J. Grant and J. Chipman—Trans. Amer.
- Inst. Min. Met. Engrs., 197 (1953) pp. 185-190.



FIG. 2- SILICON DISTRIBUTION CURVES AT 1600°C FOR LIQUID IRON-SILICON-CARBON ALLOYS SATURATED WITH GRAPHITE AND IN EQUILIBRIUM WITH LIME- SILICA-ALUMINA SLAGS UNDER 1 atm. OF CARBON MONOXIDE, ACCORDING TO J.C. FULTON, N.J. GRANT AND J. CHIPMAN.



FIG.3 - CORRELATION BETWEEN THE ALUMINA CONTENT OF SLAG AND THE SILICON CONTENT OF IRON .



Turning to the question of desulphurization, an analysis of operation data over several years shows that there is a perceptible deterioration in sulphurs with rising alumina contents, as shown by Fig. 5.

Here the casts were first grouped according to their silicon contents, and the average sulphur content of only those casts during a month, falling in any particular range of silicon, is plotted as a function of the alumina content of the slag. This method of grouping the casts were adopted to adjust for the interdependence between silicon and sulphur. The results (Fig. 5) show that for any particular range of silicon, i.e. for given conditions of temperature, intensity of reduction, slag basicity etc., an increase in the alumina content of slag tends to raise the average sulphur content of metal. This effect of alumina can be explained on physicochemical principles by reference to Fig. 6 and 7 based on laboratory investigations. It is seen that not only is the equilibrium distribution⁶ of sulphur adversely affected (Fig. 6) by rising alumina but the rate⁷ of attaining such a distribution is markedly slower (Fig. 7). It is probable that the latter influence, i.e the lower rate of sulphur pickup by the slag, is more critical in practice because it is well known that sulphur equilibrium is not attained⁸ within the blast furnace.



FIG. 6-EFFECT OF ALUMINA CONTENT OF SLAG ON THE EQUILIBRIUM VALUE OF THE DESULPHURIZATION COEFFICIENT, CALCULATED FROM THE EQUILIBRIUM DATA OF G.G. HATCH AND J. CHIPMAN-

- ⁶ G. G. Hatch and J. Chipman-ibid, 185 (1949) pp. 274-284,
- 7 L. C. Chang and K. M. Goldman-ibid, 176 (1948) pp. 309-327.

8 E. W. Filer and L. S. Darken-ibid, 194 (1952) pp. 253-257.



FIG.7- EFFECT OF ALUMINA CONTENT ON THE RATE OF SULPHUR PICK-UP BY SLAGS HAVING BASICITIES OF 108-112 , ACCORDING TO L.C.CHANG AND K.M.GOLDMAN. RATES OF SULPHUR PICK-UP ARE SHOWN FOR TWO LEVELS OF SULPHUR IN SLAG.

Effect of dolomite additions on hot-metal quality

Having discussed the effects of high-alumina slags on metal analyses, it becomes obvious that the principal objective of using dolomite in the flux is to obtain lower silicon contents in hot metal without any deterioration in the sulphur distribution. In order to study whether this was indeed achieved, the trial was divided into four periods according to the four levels of dolomite addition as follows:

Period	Dolomite in flux, % Nominal Actual		
1-30th June '57		20	20.7
1-31st July '57		30	30.3
1-17th August '57		40	41.6
18-31st August '57		25	24.3

The data collected in the trial were further supplemented by continuous operation on 7-12% dolomite during 1958 and these results are evaluated below.

A rough idea of the influence of dolomite burdens on the silicon distribution can be had from Fig. 8, where the cummulative silicon gradings of casts on all furnaces are compared during the trial period. Only the B furnace was operated with dolomite additions and it is clear that metal from this furnace was distinctly lower in silicon than that produced in other furnaces operating without dolomite. The fact that there was no such permanent tendency

for producing lower silicon metal in the B furnace during May and September proves that the observed shift to lower silicons can be attributed to the use of dolomite. Further evidence regarding the effect of dolomite on silicon distribution is afforded by Fig. 9 where the frequencies of occurrence of casts within various ranges of silicon are plotted as functions of the magnesia content of the slag. With an increase in the magnesia content, there is a significant increase in the frequency of low-silicon casts. The trends in this diagram are just the opposite of those in Fig. 4 showing a tendency towards higher silicon with rising alumina content of slag. Though the two sets of diagrams cannot be strictly compared because the points corresponding to 7-8% MgO in the Fig. 9 pertain to high-dolomite burdens resulting in a dilution of alumina to about 24.5-25%, the general trend of results proves that an increase in the magnesia content to about 5.5 or 6.0% can effectively counter the adverse influence of high-alumina.

While the first objective of producing low silicon metal is thus easily attained by adding dolomite in







OF CASTS WITH DIFFERENT RANGE OF SILICON CONTENT.

the flux, the second aim of holding down the sulphur content is also satisfied as shown in Fig. 10. In fact, it is seen that there is a significant improvement in the mean sulphur content of metal, with a given range of silicon, as the percentage of magnesia or dolomite is increased. It is probable that the major portion of this effect is caused by the greater fluidity of the high-magnesia slags. As in the case of silicon distributions, the effect of increased magnesia (Fig. 10) is opposite to that of alumina (Fig. 5), and thus operation with ε partly dolomitic burden is advantageous for the control of both silicon and sulphur.

In this discussion of metal quality, it is important to evaluate the variation in metal temperature also since this is related to the silicon content. Observations on all the four furnaces during the trial period showed that while the average temperature of the B furnace casts was about $5-15^{\circ}$ C lower than those obtained from other furnaces operated without dolomite additions, the minimum values for the B furnace were significantly lower, by about 40° C in some cases, than the minima recorded on other furnaces. These swings to lower temperatures were, however,

only accidental because later operation on partly dolomitic burdens did not show any such behaviour. It should also be mentioned here that though the lower temperature of metal may be expected to account for the greater proportion of lower silicon casts, produced with dolomitic burdening, the trend to lower silicon cannot be fully explained in this way. This is suggested by the statistical evaluation of the interdependence of silicon content and temperature during the trial run. The results showed (Fig. 11) that operation with 20, 30 and 40% dolomite in burden tends to give slightly higher silicon content for the same temperature than that found⁹ in normal practice. This may be partly attributed to the greater fluidity of the higher-magnesia slags without any significant rise in basicity.

Effect of dolomite additions on slag characteristics

The foregoing study of the influence of dolomitic burdening shows conclusively that it improves the quality of the hot metal. But similar analysis of the effects on the properties of slags would only mean restating the fundamental assumptions since



OF SILICON.

9 P. Mehta and V. G. Paranjpe-Tisco, 4 (1957) pp. 95-99.





the suggestion for the use of dolomite arises from the influence of magnesia on the liquidus temperatures¹⁰ in the system CaO-MgO-Al₂O₂-SiO₂. Slags with lower liquidus temperatures may be obtained with partial additions of dolomite. Fig. 12 shows the ternary sections at 25 and 30% Al₂O₃ representing the limits of alumina contents encountered in local operation. On these diagrams, the slag compositions obtained in normal practice, i.e. without dolomite, and during the various periods of the trial are plotted after adjusting the lime and magnesia contents to yield a total of 100% for Al₂O₃+SiO₂+ CaO+MgO. It may be seen from the sections that with normal operation, the slag composit corresponds to a liquidus range of 1,480-1,520°C with 25% Al₂O₃ and 1,500-1,525°C with 30% Al₂O₃. This clearly shows the main reason for the difficulties encountered in local practice when the alumina content increases beyond 25%. Since the actual level of alumina is about 27-28%, the liquidus temperatures for normal practice can be expected to be about 1,490-1,520°C for the quarternary slag. The presence of other oxides will lower this value by about 75-100°C; but this lowering may be taken to be approximately the same for normal and high-magnesia slags and hence only the temperatures for the quaternary system can be used for the purpose of comparison.

The effect of dolomite addition on slag characteristics during the trial may be examined from the two diagrams in Fig. 10. The positions of the points corresponding to the various stages in the trial show that the maximum lowering of the liquidus temperatures is obtained with 20% to 30% dolomite in the flux, the decrease of temperature being of the order of 40–70°C. With 40% dolomite, the liquidus temperatures are only about 10–20°C lower than those corresponding to normal practice. These observations are in full accord with the fact that burdens with 40% dolomite in the flux were not as amenable to good practice as those with 20, 25 and 30%.

As a result of the lower liquidus temperatures, the slags produced in the trial were more fluid and did not present the difficulties usually encountered with high-alumina slags.

Conclusions

An extensive trial was conducted to ascertain whether partial substitution of limestone by dolomite would offset the adverse influence of highalumina contents found in local blast furnace slags.



FIG.12-SLAG COMPOSITIONS IN NORMAL AND DOLOMITIC BURDENS PLOTTED ON THE LIQUIDUS ISOTHERMS AT TWO LEVELS OF ALUMINA.

¹⁰ E. F. Osborn, R. C. DeVries, K. H. Gee and H. M. Kraner-Trans. Amer. Inst. Min. Met. Engrs., 200 (1954) pp. 33-44.

The results proved that the addition of up to 30% dolomite gave encouraging results from the points of view of silicon and sulphur contents of metal and slag characteristics. Thus it aprears that the addition of dolomite has a special advantage with high-alumina slags compared to the comparatively lower degree of benefits derived¹¹ when the alumina contents are of the usual order of 10-20%. This special feature is obviously the direct consequence of the greater need of improving the fluidity and other characteristics of high-alumina slags.

¹¹ T. H. Kennedy and A. W. Thornton—Year book Amer. Iron Steel Inst. (1949) pp. 222–242.

DISCUSSIONS

Mr. S. R. Das, Hindustan Steel (P) Ltd., Rourkela: I would like to know if the authors have carried out any study of the coke rate by increasing the amount of MgO in the slag. Dr. V. G. Parnjpe (Author): We have studied this aspect quite a bit. In general, there is a slight increase in the coke requirement owing to the increase in slag volume. However, this alone is not the deciding factor since the overall economics is determined by the consistency of production rates, iron quality, coke rate, and other operational factors. *Mr. T. Krishnappa, Mysore Iron and Steel Works, Bhadravati*: Will the authors please let me know the alumina content before addition of dolomite and after its addition?

Dr. V. G. Paranjpe (Author): With about 40% dolomite in the burden, the alumina content went down in some cases to as low a figure as 25%, but that was the minimum. The normal alumina with 40% dolomite was about $26\cdot1$ to $26\cdot2$. With about 20% dolomite, alumina ranges between $27\cdot5$ and $27\cdot8\%$.

Dr. G. P. Chatterjee, Durgapur: I believe Tatas had an ore dressing plant to reduce the alumina: silica ratio. Could Dr. Paranjpe tell us what are the prospects of dressing such high alumia iron ores in India?

Dr. V. G. Paranjpe (Author): Much depends on the type of ore available. If Dr. Chatterjee is referring to the Naomundi ore which has a high alumina: silica ratio, I think it is fairly well known that the washing of such an ore does not lower the alumina/silica ratio because it removes more silica than alumina.

