

J. A. Charles

DURING the Symposium which was held at the National Metallurgical Laboratory two years ago, my colleague Mr. J. L. Harrison of British Oxygen Gases Limited described the conditioning of iron using oxygen prior to the open hearth furnace in his paper "Oxygen in Pyrometallurgical Techniques"¹. The merits of this process of iron pretreatment which he described then have been widely discussed before and since, and I do not think it is necessary to dwell on the advantages which can be derived or on the practice which has been established at various works throughout the world.

Although all the pretreatment methods using oxygen are metallurgically similar they differ, however, with regard to the containing vessel (i.e. its shape, the presence or absence of motion and the vessel lining that is employed) and the method of oxygen introduction which is used, these largely controlling the opportunity for adequate mixing of the vessel contents to prevent stratification of metal composition and temperature and to promote early slag formation and slag/metal contact. Stratification will reduce the speed and efficiency of desiliconisation, whilst slag/metal contact is particularly important when phosphorus removal is required. By early slag formation and good slag/metal contact dephosphorisation can be advanced relative to the removal of silicon and carbon. Further, there is the degree to which the exothermic heat liberated is conserved to give higher metal temperature.

During the last five years considerable research has been carried out on the pretreatment process at the British Oxygen Research and Development Ltd., London, S. W. 19, investigating various ways in which it can be controlled to achieve improved results in such directions as:

- (i) Control of the order in which the oxidation reactions occur—for example the early removal of phosphorus, and the retention of a higher carbon content at the end of pretreatment operations.
- (ii) Efficiency of oxygen consumption in relation to the degree of oxidation of metalloids achieved.
- (iii) Development of a process which would achieve low cost operation (e. g. high efficiency

of oxygen utilisation and a high yield of iron), require little maintenance (e. g. low refractory consumption) and which would be simple to control and whose design factors can be understood for translation to larger scales.

(iv) Production of a saleable slag as fertilizer.

As in other techniques involving the use of oxygen in the treatment of molten iron or steel there can be considerable iron oxide fume evolution with loss of yield, and possibly more important in the United Kingdom and the U.S.A., loss of face to the smoke abatement authorities! In view of the importance of this fume nuisance aspect to our steel industry much work has also been carried out by the Company on methods of iron oxide fume removal and on the prevention of fume formation, to be the subject of future publications.

The subject matter of this paper is divided into three main sections:

- (a) Investigation of ladle treatment methods with normal methods of slag-making material addition.
- (b) The tower pretreatment process.
- (c) Powder pretreatment process.

Normal ladle treatment

Much of the work in this field has already been reported elsewhere^{2, 3}. Two types of vessel were employed, holding 120–130 lb iron, a normal hand-shank open ladle provided with a refractory-lined domed cover (Fig. 1) in the earliest work, and later a specially designed bogey-mounted tilting ladle of converter shape (Fig. 2). By far the greater amount of work was carried out with this latter type.

The variables investigated included the method, rate and continuity of oxygen introduction in desiliconising without slag-making additions and the effect of slag-making additions to the melt surface under both acid and basic conditions.

Method of oxygen introduction: This work was carried out in the open ladle and the methods investi-

Mr. J. A. Charles, B.Sc., A.R.S.M., A.I.M., A.M.I.M.M., British Oxygen Research and Development Ltd., London, United Kingdom.

¹ Harrison, J. L., "Oxygen in Pyrometallurgical Techniques", Indian Mining Journal, Special Symposium Issue, 1957, 291

² Charles, J. A., Chater, W. J. B., and Harrison, J. L., "Oxygen in Iron and Steel Making", Butterworths Scientific Publications Ltd., London, 1956.

³ Charles, J. A., and Churcher, T. C., "Use of Oxygen for Pretreatment of Molten Iron—Some Small-Scale Experiments under Acid and Basic conditions", Iron and Coal Trades Review, March 22nd 1957, 174, 4635, 667-672.

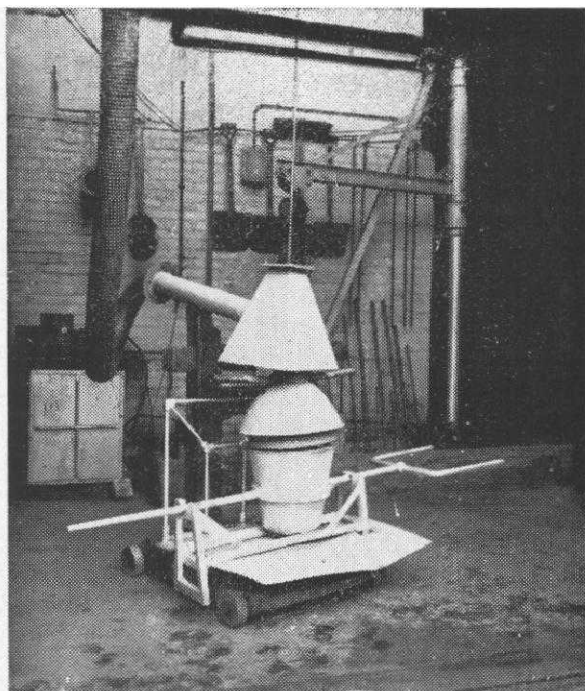


Fig. 1.
Early Ladle Treatment equipment.

gated were: lancing beneath the metal surface with 0.3125 (5/16) in. bore steel pipe, jetting on to the metal surface with a 0.3125 (5/16) in bore pipe, a 0.1094 (7/64) in. bore nozzle and a 0.076 in. throat convergent-divergent nozzle, giving subsonic, sonic and supersonic oxygen jets respectively, all at oxygen flow rates of 10 cft./min. In all the jetting tests the probe was protected by a suitable refractory coating.

Although the difference between the jetting methods was not as great as might have been expected, in high silicon ranges (above 1.8%) the use of the low velocity jetting method (i.e. using 5/16 in. bore pipe) gave slightly higher efficiencies (i.e. quicker arrival at a required silicon concentration with less oxygen consumed) than the other methods. With decreasing silicon concentration high velocity jetting became more efficient until at low levels the supersonic jet gave the best results. The variation that does exist between jetting methods appears to be directly connected with the two main factors of penetration area and penetration depth. In the initial stages of blowing at high silicon concentration the governing factor is the area of penetration since the metalloid concentration at the surface and the diffusion potential towards the surface is still high. In the later stages of silicon removal turbulence becomes of greatest importance so that the metalloids can be continuously brought into the zone of reaction. This turbulence occurs to a greater extent with the high velocity oxygen streams which penetrate more deeply. At

the same time a natural consequence is that there is a greater metal loss by ejection and spillage and reduced metal yield. The carbon loss accompanying desiliconisation also appeared to be greater when operating with high velocity jets. In lancing, the initial desiliconising efficiency was higher than either sonic or supersonic jetting, although not as high as with sub-sonic jetting, and the efficiency remained more constant over the complete range of silicon removal.

Rate of oxygen introduction: Within the conditions of our experiments the rate of oxygen introduction did not have any appreciable effect on the final silicon content reached for a given quantity of oxygen introduced, provided it was sufficiently high to generate enough heat to counter the heat loss from the vessel and the rise in the liquidus temperature, i.e. sufficiently high to prevent the melt solidifying.

Continuity of oxygen introduction: It was quickly noticed that in jetting with oxygen considerable stratification occurred, both of metal composition and metal temperature. As an example of this effect, a sample taken from the melt surface immediately after low velocity oxygen jetting, with the minimum turbulence imparted to the metal contained 0.17% Si whereas the average analysis of the bath after stirring showed 1.31% Si. For this reason, it was anticipated that where the progress of a jetting operation was interrupted for sampling and temperature measurement high desiliconisation efficiencies would result, since the silicon potential in the metal adjacent to the

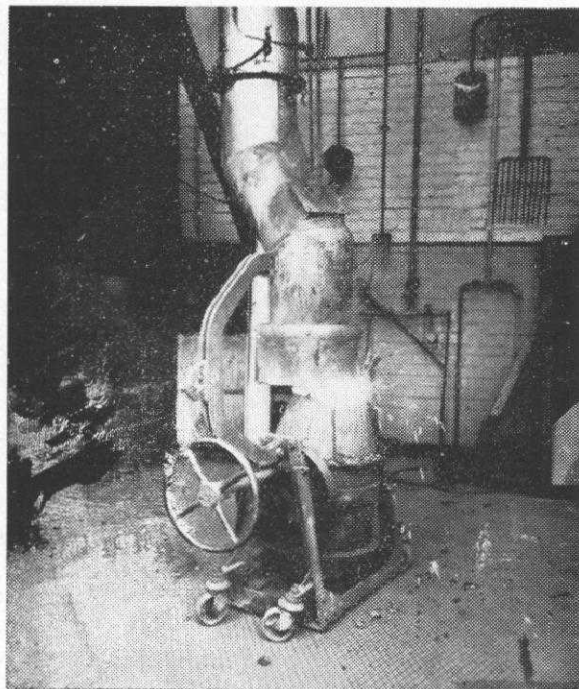


Fig. 2.
Improved equipment for Ladle Treatment.

point of oxygen introduction would be raised by diffusion and the mechanical agitation involved in sampling. This was shown to be true, and although the differences were not great, continuous operation generally resulted in less efficient desiliconisation in terms of the amount of silicon removed for a given quantity of oxygen introduced, than where the blow was interrupted for sampling. The effect was relative to the amount of turbulence created in the melt by the oxygen stream. With the more general agitation caused by deep lancing (practicable on this scale) stratification did not occur and there was no difference between continuous and discontinuous operation as regards the final silicon content.

Effect of slag-making materials under acid conditions: Surface additions of slag-making materials were made with the intention of improving the efficiency of silicon removal, and in the hope of simultaneously removing phosphorus. It is well known that these objects can be achieved by the addition of iron oxide and limestone in basic ladles, but obviously in the presence of acid refractories serious lining attack with reduction in slag basicity and dephosphorising power would occur, the effect increasing with temperature. For this reason interest was mainly centred on soda ash, which is generally considered a more stable dephosphorising agent in the presence of siliceous materials. Melts were, however, carried out with limestone/iron ore slags as a means of comparison. The effect of temperature was investigated by allowing melts to cool between intervals of blowing. Fig. 3 shows that at low temperatures (metal allowed to fall below 1,300°C between blowing periods) phosphorus can be removed at silicon contents as high as 1% with soda ash, but only below 0.5% when using limestone/iron ore. At high temperature (rising to 1,500°C during the blow) phosphorus can only be removed by soda ash, and then only at silicon contents below about 0.5%. With limestone/iron ore additions the lining attack at the high temperatures rapidly reduces the slag basicity and no dephosphorisation occurs. Some increase in desiliconisation efficiency resulted with both additions and soda ash gave useful desulphurisation.

Soda ash is, however, not a particularly attractive material to use in the steel industry because of its effect on refractories at high temperatures in subsequent steel making processes and because the slag formed during pretreatment is difficult to remove completely. This work has not, therefore, been taken further, and is included only as a matter of interest.

Effect of slag-making additions and other variables on operation under basic conditions: All this work was carried out in the converter-shaped ladles lined with dolomite and with refractory-coated lances. Jetting was attempted but proved less satisfactory on this small scale owing to the difficulty of judging the depth of the jetting probe in the slag and consequently its distance from the metal surface. Both soda ash and limestone/iron ore additions were investigated but soda ash offered no

advantage in silicon and phosphorus removal under basic conditions.

Oxygen pretreatment for silicon removal alone would obviously be normally carried out in an acid-lined vessel. Under the more expensive basic lining conditions early, if not simultaneous, phosphorus removal is of prime interest. Using a wide range of irons it was found possible to obtain considerable dephosphorisation during and immediately following silicon removal to give low phosphorus contents, at the same time maintaining the carbon content in the 1.5-2.0% range. Fig. 4 indicates the results obtained on what we considered to be a typical Indian-type iron containing 1.5% Si and 0.4% P.

With higher initial phosphorus contents dephosphorisation tended to be earlier and more rapid, so final phosphorus contents of a similar order were obtained without greatly increased quantities of oxygen being required. During the progress of blows on the Indian iron to give phosphorus contents below 0.10% the temperature rose from about 1,250°C to 1,450°C. It must be admitted that this starting temperature was a little low in comparison with blast furnace iron temperatures, but it quickly rose to 1,350°C during the initial desiliconisation. That the practice is feasible under full scale conditions was later demonstrated by Brymbo Steelworks Limited⁴.

The Tower pretreatment process

During the course of the early work in our laboratories on iron pretreatment the idea of a continuous system in which the iron was introduced down through an atmosphere of oxygen confined in a refractory tower structure developed and in 1955 practical work commenced. Work has been actively in progress since then, initially under my own supervision but in more recent years by my colleague Mr. T. C. Churcher. A full report of the process, as developed up to March 1957, was given to a private conference for British steelmakers held by the British Oxygen Company Limited at Ashorne Hill, Leamington Spa, England, in that month. It is of interest to note that recently a paper was published by Gaines and Hilty of Union Carbide (Linde Company)⁵ describing the early stages of their work on an almost identical process in the U.S.A.

The aim behind the development of the tower system was to operate a semi-continuous process which would not be subject to difficulties such as melt stratification and which would provide for more rapid and efficient pretreatment with reduced refractory wear. Since the reaction occurs in a confined space it was also hoped that any carbon monoxide

⁴ Davies, E., "Pre-refining of Blast-Furnace Iron with Oxygen", Iron and Coal Trades Review, 1956, 172, 4595, 987-988.

⁵ Gaines, J. M. and Hilty, D. C., "Hot Metal Pretreating Tower", Journal of Metals, July 1958, 10, 452-455.

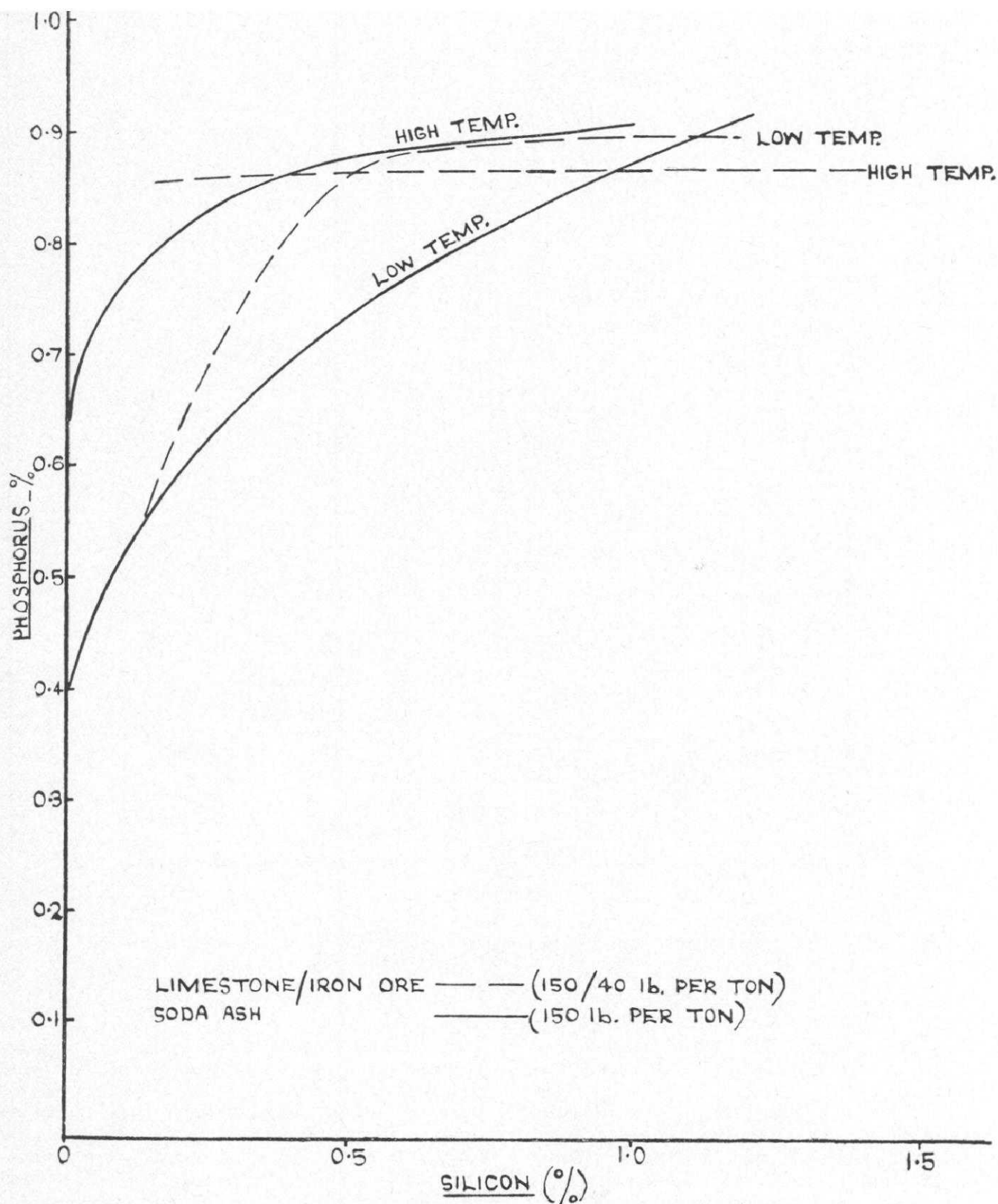


Fig. 3.
Relationship between Silicon and Phosphorus. (Acid conditions.)

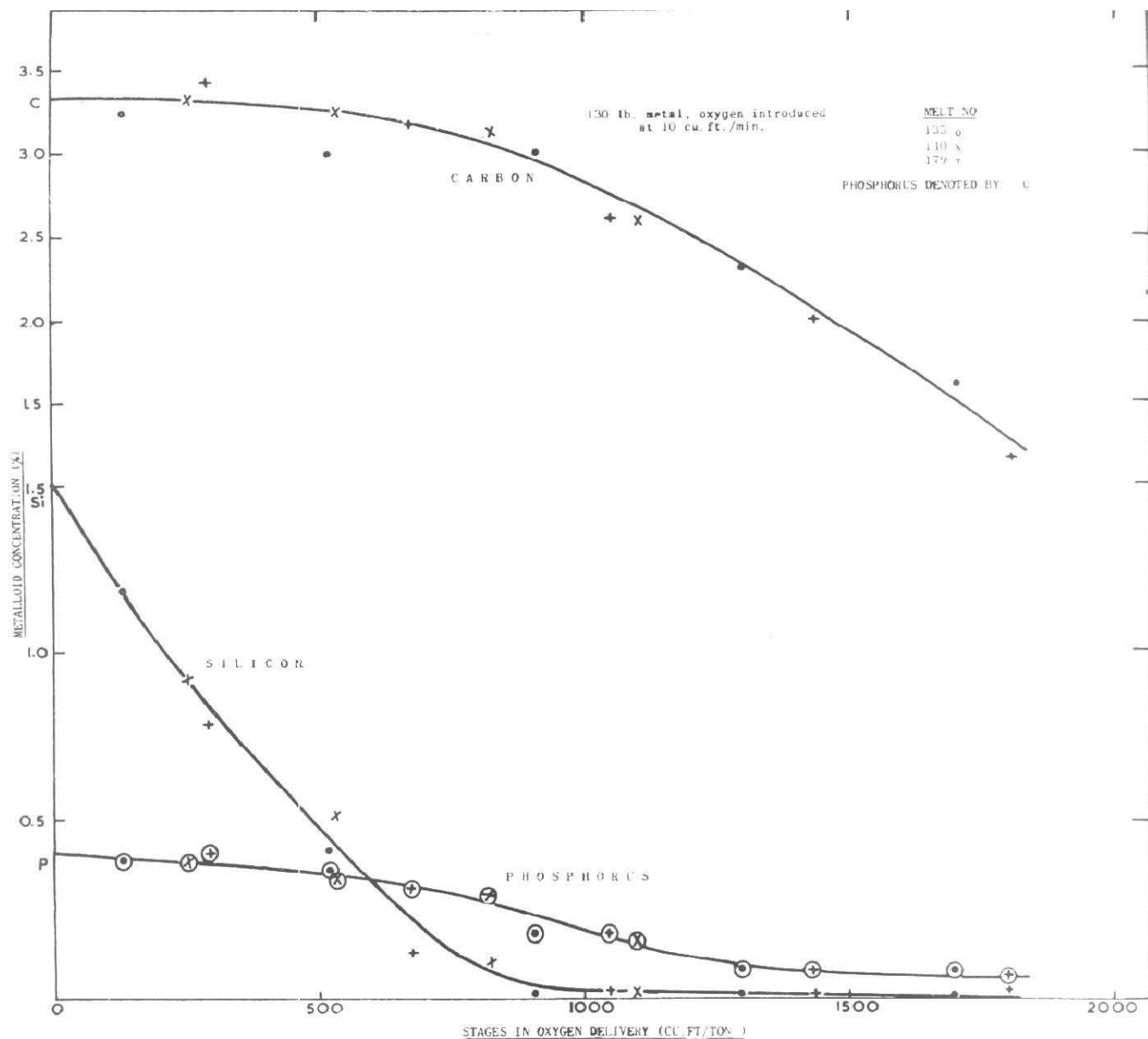


Fig. 4.

Variation of metalloid concentration with oxygen tonnage rate. Limestone/Iron ore mixture additions. Single Slag. (150/40 lb per ton)

produced by carbon oxidation would subsequently burn and give a higher heat yield to the metal than in an open ladle.

The present design of the unit in our research laboratory is shown in Fig. 5. The refractory-lined steel drum column is 9 ft. high and 8 in. internal diameter. The lining consists of an outer layer of high temperature insulation bricks and an inner working lining of magnesite-chrome concrete. Four water-cooled oxygen tuyeres, radially opposed, are

located a little below the streaming crucible or tundish. A further set is also provided lower down should they be required. The streaming crucible is provided with a removable refractory sieve or distributor (sillimanite nozzles set in an aluminous cement) containing a number of $\frac{1}{4}$ in. diameter holes.

The whole column is preheated to about 1,100°C by means of air/coal gas burners, one located near the top streaming crucible and the other inserted in the bottom pointing upwards.

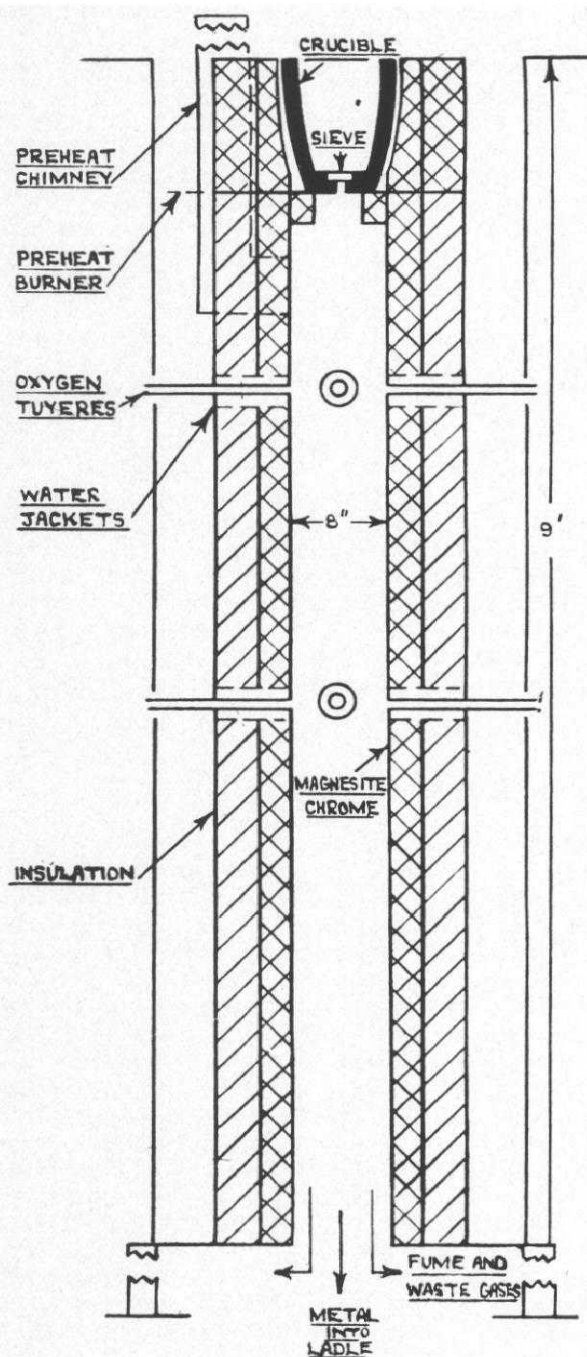


Fig. 5.

General arrangement of the co-current Tower apparatus.

Fig. 6 shows iron being poured into the streaming crucible at the top of the tower and Fig. 7, a general view of the equipment.

The following details are taken from a typical pour, showing the kind of result that can be obtained with the apparatus in straightforward desiliconisation:

No. of metal streams ... 2
Diameter of metal streaming holes $\frac{1}{4}$ in.

No. of tuyeres operating ... 4
Metal pouring rate ... 1 cwt/min.
(approximately)
Oxygen introduction rate ... 1,100 cft/h
Equivalent oxygen used ... 402 cft/ton
Metal temperature at start ... 1,415°C
Metal temperature at finish ... 1,435°C ($4\frac{1}{2}$ min.
after pouring)

Analysis of metal		Before	After
C%	...	3.67	3.57
Si%	...	0.78	0.06
Mn%	...	1.06	0.36
P%	...	0.67	0.61
Iron in slag %	...		22.2
Iron loss as fume %	...		0.31
Efficiency of oxygen usage	...	78%	
Yield of metal	...	96%	

Experiments on our small scale have shown that the most efficient operation can only be achieved if the iron being poured is above 1,350°C but lower values may be acceptable on a larger scale since heat losses from the system will be very much reduced. Up to $\frac{1}{4}$ in. diameter the size of the holes in the streaming sieve does not seem to greatly affect the desiliconisation efficiency, but with larger

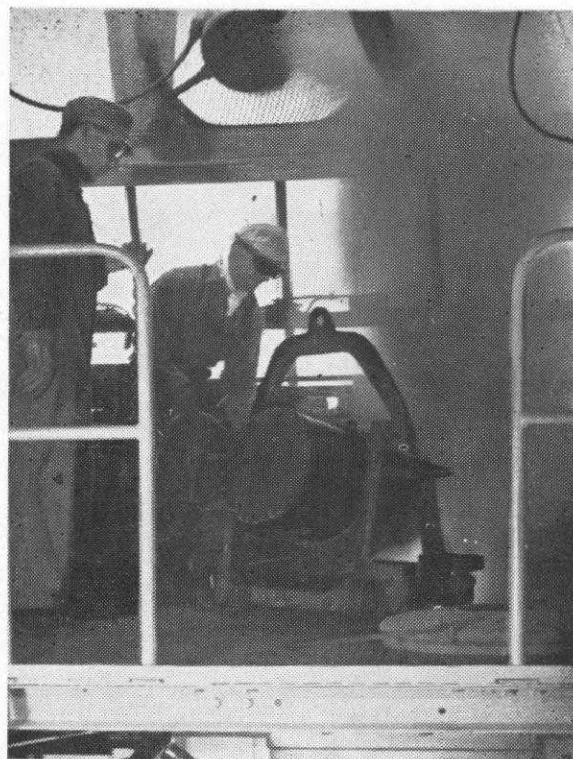


Fig. 6.

Iron being poured into the top of the Pretreatment Tower.

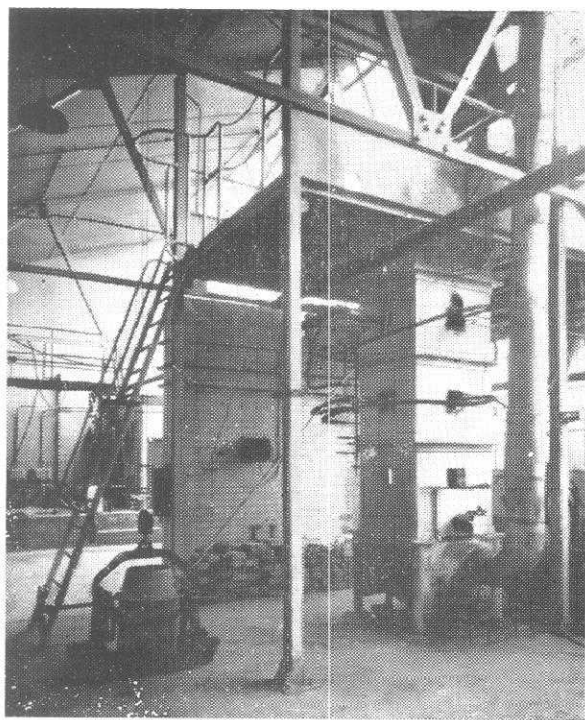


Fig. 7.
General view of Pretreatment Tower.

holes the size of droplet formed has been shown to increase significantly, with reduced reaction during the period of fall. The metal yield values and the iron contents of the slags obtained compare favourably with lancing in the ladle for the same result on similar weights of metal. Refractory wear in the column itself is negligible since there is virtually no metal contact and maintenance is restricted to the streaming crucible and the replacement of the sieves.

Recent work has involved the addition of lime in the tower system to achieve full pretreatment of the iron (i.e. both silicon and phosphorus removal). The lime addition was made in two main ways, either added as lumps to the receiving ladle catching the iron beneath the tower, or else dispensed as powder with the oxygen into the column itself. Dispensation appears to give the best results and the details of a typical pour are given below:

Metal temperature before	...	1,415°C
Metal temperature after	...	1,420°C
Oxygen introduction rate cft/ton	...	820
Lime rate lb/ton	...	40.3
Metal yield	...	90%

Analysis	Before	After
C%	3.78	3.12
Si%	0.63	0.01
Mn%	1.23	0.15
P%	1.04	0.66

Blowing at higher rates gives still lower phosphorus

values, but the carbon content is also, of course, further decreased.

From our work we feel that this process should achieve industrial application. The reactants are brought into intimate contact over a large moving surface area, so that reaction is very rapid and relatively unhindered by any concentration gradients in the metal phase, and as compared to other methods of continuous treatment, such as special launders, it offers the advantage of minimised refractory/metal contact and thereby reduced refractory wear. As far as operation is concerned we have found it to be more convenient and simple than ladle treatment. The main difficulty which is likely to occur is in the provision of sufficiently robust and easily replaceable sieve discs in the streaming crucible or ladle. This and other full scale practical problems are being investigated on a pilot scale with equipment installed at the Consett Iron Company Limited and we would like to take this opportunity of gratefully acknowledging their co-operation in this venture. Our laboratory equipment is normally operated at a rate equivalent to 3 tons of metal treated per hour, on occasions increased to 10 tons per hour. The pilot plant at Consett is capable of extending this to a rate of 60 tons per hour, using 20-ton batches of metal.

Powder pretreatment process

A great deal of our work carried out in this field has been reported by Cook⁶. Lime, iron ore and flux (fluorspar or bauxite) powder were dispensed with the oxygen into the melt through the oxygen lance. Substantial amounts of dephosphorisation were achieved even in acid-lined vessels, but the powder consumption and ladle lining wear in this case were excessive. Under the more practicable basic-lined vessel conditions a single slag treatment was developed for irons of moderate phosphorus content, enabling low levels of residual phosphorus content to be obtained with ease. For irons of higher phosphorus content a double slag treatment was employed, which, with the incorporation of bauxite as the flux, enabled a slag of saleable composition to be produced. Such a double slag technique is generally necessary in pretreatment processes involving phosphorus removal from phosphoric irons if a slag sufficiently high in P_2O_5 for use as a fertiliser is to be produced generally a minimum citric acid soluble P_2O_5 content of 13% is stipulated and the use of bauxite as a flux is preferred to fluorspar since it does not lower the citric acid solubility of the phosphate.

The general arrangement of the equipment used is shown in Fig. 8. As in the other ladle treatment work described the lance used was of 5/16 in bore, the oxygen being introduced at 10 cft./min. The lances were, however, uncoated so as to exclude any effect refractory protection might have on the

⁶ Cook, L., "Pretreatment of Molten Iron-Desiliconisation and Dephosphorisation Experiments", Iron and Coal Trades Review, July 11th 1958, 177, 87-93.

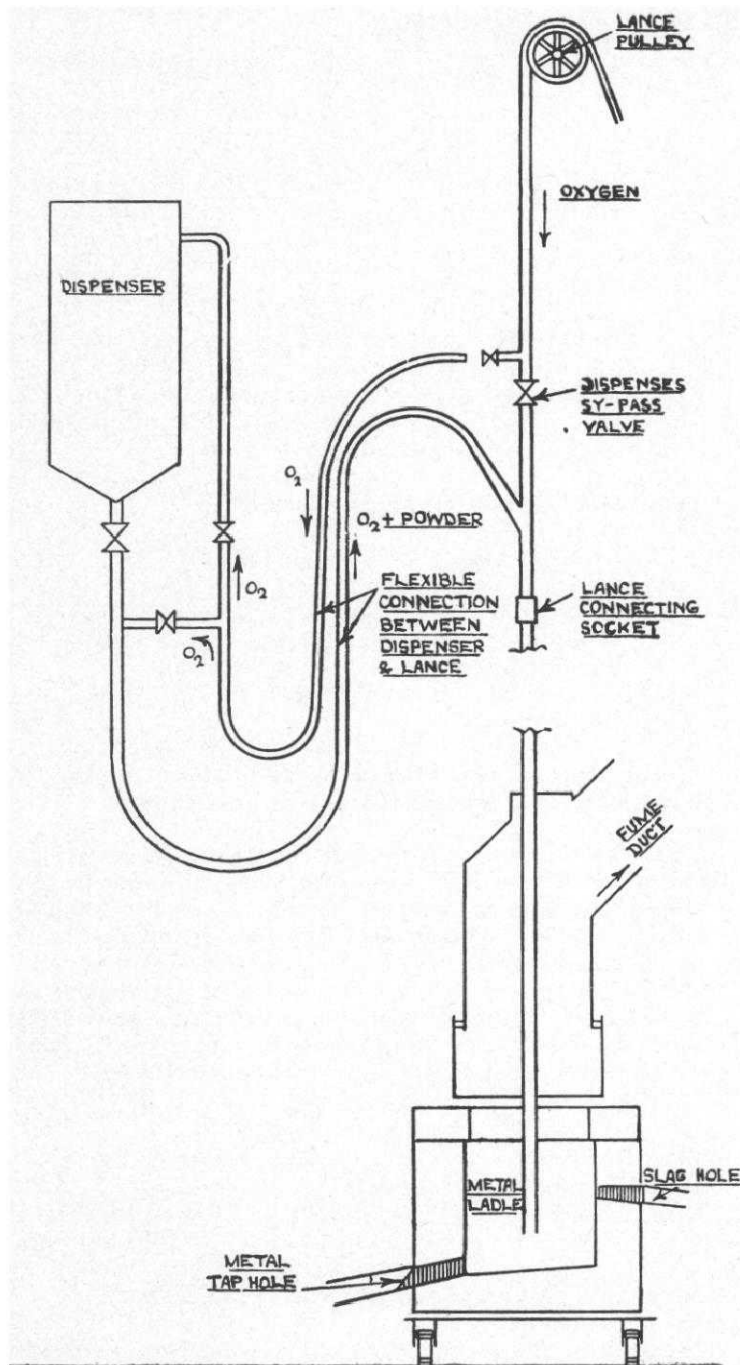


Fig. 8.
Dispensing equipment.

slag composition, which could be considerable on this small scale. In full scale practice it is anticipated that refractory coatings or water cooling would have to be employed.

As indicated above various types of treatment ladle and slag mixtures with double and single slag practice were employed in the investigations, but it will suffice here to report the average results that

were obtained using a single slag in a magnesite-chrome lined ladle by the injection of a powder mixture containing 5 parts burnt lime, 5 parts millscale and 1 part fluorspar with the oxygen:

Initial metal weight-lb ...	111		
Stages in oxygen blowing at 10 cft/min-min. ...	0	3	6
Cumulative oxygen delivery equivalent cft./ton metal (initial weight) ...	—	605	1,209
Wt. of powder added in stages lb. ...	—	9.1	9.1
Cumulative delivery of constituents, lb/ton metal (initial weight)			
Lime ...	—	83	167
Millscale ...	—	83	167
Fluorspar ...	—	17	33
Metal Analysis %			
C ...	3.57	2.86	1.72
Si ...	0.79	0.08	0.02
Mn ...	0.63	0.09	0.07
S ...	0.106	0.098	0.052
P ...	1.13	0.59	0.026
Slag Analysis %			
SiO_2 ...	—	14.8	7.0
CaO ...	—	31.4	39.8
P_2O_5 ...	—	12.8	14.3
Total Fe ...	—	21.1	23.7

Metal temperature rose in the range 1,425–1,550°C.

As well as the complete dephosphorisation achieved with moderate oxygen input and the retention of a substantial carbon content it is notable that appreciable sulphur removal was also effected. From our results it would appear that the use of oxygen-borne powdered slag-making materials gives more rapid and reproducible dephosphorisation than is possible by surface additions. This is because the materials are introduced in a finely divided state into the high temperature oxidation reaction zone where they can rapidly flux and combine with the products of oxidation. For this reason it would seem likely that an even greater differential in efficiency would be obtainable on a large scale where there would be less gross turbulence in the vessel during normal lancing with surface additions than on our small scale and where slag reactions would have to proceed to a greater extent by diffusion processes across the normal slag/metal contact surface.

The intention in this paper has been to give a broad picture of some of the lines of research which have been followed by B.O.R.A.D. in the field of iron pretreatment. Intensive work continues both in this field and in many others involving the use of industrial gases in metallurgical processes, for with each succeeding year the scope widens and we intend to do our part in ensuring that technical development in the British Commonwealth does not fall behind the rest of the world.

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