Chemical Reactions of Iron Smelting*

A Review of Processes as Carried on Today

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THROUGHOUT the Middle Ages, and as late as the first half of the nineteenth century, blast furnaces were operated the world over with the utmost of secrecy. Those skilled in the art carefully guarded their knowledge, surrounding their work with a veil of mystery and handing it down from father to son as a precious tradition.

There are still many adherents to the creed that blast furnace progress must be brought about through practice, leaving it to science to afterwards explain the "whys and wherefores." Men of this type overlook the fact that, since the introduction of hot blast, when explanations were sadly lacking for the startling improvement wrought thereby, science has made gigantic strides to close the gap between actual results and their theoretical understanding. As the day draws near when the scientist will wring from the blast furnace his last mystery and will mark it down with mathematic exactness, the theory of the blast-furnace process demands of the furnace operator more respect and attention than ever before. While he may not care to follow all the intricate lanes of research and experimentation that have led to the present knowledge, he should have a thorough understanding of the process with which he deals, and it is from his standpoint that I intend to review the reactions of iron smelting as carried on in the blast furnace of today.

PHYSICAL AND CHEMICAL DUTIES

The task of the blast furnace, while performed as one continuous and interlocking process, may be divided into physical and chemical duties. Among the former the principal items are:

The drying and preheating of the burden materials.
The melting and superheating of the resultant iron and slag.

The chemical duties comprise chiefly the following:

The calcination of the carbonates.
The reduction of the metallic oxides of the ore burden.
The relative importance of the physical and chemical work may be best judged by comparing the amount of energy consumed by each. This can readily be calculated by establishing a heat balance.

An average taken from a number of such calculations covering modern operations shows that, of the total heat introduced into a blast furnace and generated therein, approximately 25 per cent is sufficient to take care of the above-mentioned physical duties, while the chemical reactions require about 60 per cent of the total, the balance being absorbed in radiation losses and heat escaping with the gases. These figures gain particular interest when considering that it is the physical part of the blast furnace work only that is immediately accessible to observation and measurement. Any improvement or deterioration in the chemical work must affect the furnace efficiency as a whole to more than double the extent than would a change of equal magnitude in the physical or melting operation. Economy in the performance of the chemical reactions is, therefore, of prime importance to the blast furnace man.

From the total amount of coke which is charged into the blast furnace, a certain percentage is always carried out by the furnace gases as coke dust, and another portion is dissolved by the pig iron. At plants using similar raw materials, and under normal operating conditions, the sum of these two items varies only within narrow limits and amounts to a small percentage of the total. It does not decidedly influence the general efficiency of the furnace operation. The fuel consumption depends almost exclusively on the mode of gasification and utilization of the remaining major portion of the carbon in the coke. The possibilities in this respect are:

1. The carbon, having passed downward through the furnace stack, reaches the hearth and is gasified there either by:

- (a) Combining with the oxygen of the blast at the tuyeres, or
- (b) Combining with the oxygen of metallic oxides (direct reduction).

2. The carbon does not reach the hearth, but is gasified above the hearth by reacting with the CO₂ of the furnace gases (premature combustion).

The reactions classed under 1 are normal operating

necessities. Reaction (a) creates heat and reducing gas (CO); reaction (b), while consuming heat, furnishes reducing gas and pig-iron product. As long as their sum total and their relative proportion remain within proper limits, these reactions must be classed as desirable, while an excess of either one is superfluous and detrimental.

The reaction named under 2 produces, at a loss of heat, reducing gas only, which, if at all required in the operation of the furnace, could be more advantageously furnished by either reaction 1 (a) or 1 (b). The premature combustion of carbon must, therefore, in all cases be considered a detrimental reaction.

All three of these reactions have one thing in common. They produce carbon-monoxide, the agent by means of which by far the largest portion of the metallic oxides in the furnace burden is reduced to metal. This process, for which the equation $\text{Fe}_2\text{O}_3 + 3\text{CO} = 2\text{Fe} + 3\text{CO}_2$ may serve as an example, is known as "indirect reduction." Its economy is in a large measure responsible for the remarkable efficiency of the blast furnace, which to the present day has not been surpassed by any other metallurgical process.

INDIRECT AND DIRECT REDUCTION

From a standpoint of economy, the indirect reduction is more desirable than the direct reduction. The latter is economically permissible only under the following conditions: First, where indirect reduction cannot take place—for instance, when reducing oxides are not accessible to furnace gases; and, second, in case the combustion of carbon by the oxygen of the blast at the tuyeres does not furnish sufficient carbon monoxide with which to properly take care of the indirect reduction.

Direct reduction, as mentioned first, takes place in every furnace and is a function of the composition of the iron; in other words, the percentage of silicon, phosphorus, manganese, etc., to be reduced and of the percentage of burden materials, the metallic contents of which are for physical or chemical reasons not accessible to the reducing action of the furnace gases. With these conditions given, this phase of direct reduction can be considered as practically constant.

The other case of direct reduction, which is due to scarcity of CO from combustion at the tuyeres, is most likely to be incurred where furnaces are burdened with ores that are easily reduced, and where such furnaces are operated at a fast rate of driving, with high-blast temperatures. Under such conditions, direct reduction will take place to a greater extent the lower the percentage of silicon is in the pig iron. Modern Mesaba practice on basic iron is a good example.

The extent to which the various reactions will perform within the blast furnace depends in a large measure upon the reacting speed of which they are capable. The speed of any chemical reaction decreases the closer the relative quantities of the reacting and resulting substances approach the status of equilibrium. Therefore, various reactions will, within the limited time available in the blast furnace, take place to a larger extent the farther away the relative quantities remain from the status of equilibrium. In other words, in order to be reducing to a degree sufficient for actual practice, the furnace gases must be richer in CO than would be expected from the experimentally determined diagram of Baur and Glaesner.

Thus the possibility of a modern furnace being insufficiently supplied with carbon monoxide through the combustion of carbon at the tuyeres is by no means remote. It is incurred particularly where, with easily reduced ores, high blast temperatures are used, because with higher blast heat the generation of the necessary quantity of heat in the hearth requires less carbon. Theoretically, and keeping strictly within the boundaries of Gruner's theory of the ideal working of a blast furnace, this condition should be remedied by lowering the blast temperature and burning more carbon at the tuyeres. Otherwise, ore must reach the hearth without being properly reduced by the gases, there to be reduced by solid carbon, with a consequent loss of heat to the hearth.

In modern practice this question is solved differently and more economically by permitting direct reduction to take place and at the same time offsetting the entailing heat loss by raising the blast temperature. The limit to which this direct reduction can be carried on depends on the ability to offset the resultant heat deficit in the hearth by higher blast temperature, and on the necessity to keep the top temperature above the

desired minimum which is essential for the timely drying and preheating of the ore charges preparatory to their reduction by the furnace gases.

The results obtained may briefly be summed up as follows: Without raising the volume of wind blown, the amount of carbon gasified in the hearth and the weight of metallic oxides reduced per unit of time is increased. The furnace operates at a higher rate of output without requiring additional coke for its hearth reactions. As the cooling and radiation losses per ton of iron are inversely proportional to the rate of production, a saving is effected in this respect, which must ultimately find its expression in a lower coke consumption. As a part of the coke carbon is gasified by oxygen from the ore without the addition of nitrogen from the blast, the amount of gas per unit of burden material charged becomes less. The initial temperature of the gas leaving the hearth not being changed, this results in a lower top temperature as well as a lower temperature of the stack. The beneficial effect of this drop in stack temperature on coke consumption and on furnace practice in general will be dealt with later.

PREMATURE COMBUSTION

At temperatures below 900 to 1,000 deg. C. premature combustion does not take place to any appreciable extent, as can readily be seen from the curves of equilibrium established by Bondouard. Since its reacting speed grows rapidly with rising temperatures, it is evident that premature combustion must take place in the furnace stack at an increasing rate the higher the temperature of the zone in which the carbon dioxide and the coke come into mutual contact and the longer they remain in contact with each other at temperatures above 900 deg. C.; that is, generally speaking, the higher the average stack temperature of the furnace happens to be. Thus it occurs to a large extent in furnaces making high silicon iron, or furnaces operating on a highly refractory burden, for instance, of magnetite ores. Under such conditions, carbon monoxide is produced over and above the already existing abundance, which has resulted from extensive direct reduction, and which cannot be used to any advantage in the furnace.

In furnaces producing low silicon iron and operating on an easily reduced ore burden, premature combustion may also assume serious proportions, where the rate of driving is too slow and the time is thus unduly prolonged during which carbon dioxide remains within the regions of high temperature in contact with coke. The apparently logical means of counteracting this condition is "faster driving." In many cases this can only be practised after a change in the quality of coke has been brought about.

Among the ways and means which counteract premature combustion and are practised, aside from faster driving, I wish to mention one which is now so universally used that its value is often overlooked. I refer to the use of raw limestone as flux. Realizing that it took a considerable amount of heat to calcine the stone, and in an effort to relieve the blast furnace of this duty, the attempt was repeatedly made in past days to charge burned lime in the place of raw stone, but without attaining the expected improvement.

The explanation lies obviously in the fact that the endothermic calcination of the limestone, which takes place above 900 deg. C., is one of the most effective means to quickly bring about a cooling of the furnace gases below the zone of temperature where premature combustion can take place; it appears that thereby, and by simultaneously preventing premature fusion of the ores, which would place the latter beyond the reach of indirect reduction, more coke is preserved and made available for the generation of heat at the tuyeres than is necessary to furnish the heat required for the calcination of the stone.

Another most effective means of preventing premature combustion is the application of high blast temperatures. By thus accelerating combustion at the tuyeres, providing for the heat requirements of the hearth with less fuel and a consequently lower volume of gases, concentrating the zone of highest temperature and increasing the ratio of descending materials to rising gases, a decided lowering of the average stack temperature with correspondingly better fuel economy can be and has been accomplished. For instance, the blast furnaces at South Works, Illinois Steel Company, being operated according to these principles, have for

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a number of years, in spite of a severe handicap in the form of irregular coke supply, not for a single month exceeded a coke consumption of 1,900 pounds per ton of iron for 21 consecutive months. During the year 1916, these same furnaces, with an average age of 331,771 tons per lining, produced 2,066,246 tons of iron on an average coke consumption of 1,854 pounds per ton.

From the analysis of the various reactions, it is evident that direct reduction and premature combustion in reference to origin, performance and prevention are two distinctly and entirely different processes, each one independently playing its own important part, in widely varying degrees, in every furnace operation. The only common tie between them is their endothermic character and the fact that they both consume carbon. The sum total of their carbon consumption represents what is usually called the amount of carbon gasified above the tuyeres. As this carbon is consumed partly by economical and partly by wasteful reactions in ever varying proportions, it is evident that the relation of this total "carbon gasified above the tuyeres" to the fuel consumption of a furnace cannot possibly have a direct bearing on the economy of the furnace operation.

CARBON DEPOSITION

To complete this review of blast-furnace reactions, I wish to mention one which in modern furnaces appears only occasionally to any extended degree. This

is the decomposition of carbon monoxide according to the equation $2CO = C + CO_2$.

As the speed of this reaction is comparatively low, on account of the existing ratio of quantities involved, and since the zone of temperatures within which it can take place is limited to approximately from 400 to 600 deg. C., the extent of this reaction is, as a rule, slight. Theoretically it must be classed as economical, being exactly the reverse from "premature combustion." However, in practice, when this reaction takes place to any considerable degree, serious difficulties are encountered which make it extremely undesirable. The resulting carbon is deposited on the ores in a very finely divided form and interferes with their permeability to the gases, clogging the voids and causing a swelling of the charges, scaffold formation and all the serious troubles which follow.

When fine Mesaba ores were first used in larger percentages, such difficulties due to excessive carbon deposition were experienced more frequently. With furnace lines poorly suited for the smelting of these fine ores, particularly with the flat bosh angles then in use, irregular working of the furnace with protracted periods of hanging were nothing exceptional. The movement of the furnace charges being brought to a standstill for considerable periods of time, a much larger percentage of the materials in the upper part of the furnace stack was heated to a temperature where

decomposition of carbon monoxide could take place, with a corresponding increase in the extent of this reaction as the result. Since then, however, furnace lines have been improved to such an extent as to make operating difficulties from this source a rare exception in Mesaba practice.

It has been observed, too, that a high percentage of hydrogen is often present when carbon is deposited in this manner. The reducing power of hydrogen relative to that of carbon monoxide increases with falling temperatures, and it is reasoned that, with a high percentage of the former, metallic iron in finely divided form is reduced from the ores at exceptionally low temperatures; this metallic iron then acts as a catalytic agent which greatly increases the reacting speed of the decomposition of carbon monoxide.

Excessive hydrogen in the top gases to an extent necessary to bring about such a condition is generally the result of defective apparatus, such as leaky hot-blast valves, tuyeres and bosh plates. If this be the case, the undesirable deposition of carbon can be overcome by removing the source of the hydrogen.

From the standpoint of an operating man, I have attempted to give a brief outline of a subject about which volumes have been written by men of science without ever covering the field. To them belongs the task of further theoretical exploration. We blast-furnace operators must be ready to apply and prove in practice.

Aluminium

ALUMINIUM is a material in which practically every owner of a motor car is interested. As most of us know, or knew once, aluminium is of extraordinary prevalence in nature, and is more abundant than any other metal, as it is said to constitute about 8 per cent of the earth's crust. So far as present indications go, it would appear that the motor car will become more and more like nature, inasmuch as it will consist to a larger extent than it does today of aluminium suitably alloyed with other metals. Interesting as aluminium may be to the motorist today, it appears that it will be still more interesting to him a few years hence. It certainly will be if the aluminium air-cooled engine should become prevalent.

When aluminium was discovered by Michael Faraday in 1827 he had no idea what he was building up. As Mr. E. Carey Hill pointed out in his paper on "Aluminium in the Motor Industry" read before the Coventry Engineering Society recently, twenty-seven years elapsed before aluminium was obtained in a perfectly pure condition. There is no doubt that the early aluminium was very tricky and unsatisfactory from a manufacturing point of view. It was stoutly maintained by many of the old school of engineers that aluminium was dirt electrolytically persuaded to become a metal, but ever ready to revert to its original state, and therefore they placed no faith whatever in it.

However, as Mr. Hill pointed out in his paper, from 1906 onward a vast amount of scientific research has been conducted in connection with aluminium, and some of the results are given in the periodical reports of the Alloys Research Committee of the Institution of Mechanical Engineers. Mr. Hill suggested that still greater advances had been made since the outbreak of war, as aluminium plays so important a part in the construction of the aeroplane that it has been a constant subject of research at the National Physical Laboratory and elsewhere. The full results of these later researches and experiments can only be dealt with after the war.

As everyone knows, the outstanding property of aluminium is its lightness; in its pure state it is only slightly above one-third the weight of iron, volume for volume. It is too soft to be used in engineering design unalloyed, but when alloyed this softness is corrected and its density considerably increased. It does not corrode at all readily in its pure state, and even when alloyed a dry atmosphere has practically no effect upon it. One of the most difficult aspects of its handling in the foundry is that its contraction during cooling is rather high, amounting to about three-sixteenths of an inch to the foot, and this property creates a number of difficulties which the art of the founder has to overcome.

It is probably not generally known that aluminium has been adopted in the electrical world to replace copper in large insulated cables for power transmission, as although its electrical conductivity is only 58.5 as compared with copper 97.5, yet, as its weight is less than one-third that of copper, volume for volume, this is no detriment, and, speaking roughly, an aluminium cable of equal conductivity to a copper cable would be 50 per cent lighter so far as its metallic portion was concerned.

Foundry experience has taught aluminium casters that there are certain main principles that must be adhered to, even with alloys, if good results are to be obtained systematically, and the factors which govern

these principles are (1) the high contraction of aluminium during cooling, (2) the peculiar stage of plasticity through which it passes between liquid and solid, similar to common solder; and (3) its very low density at high temperatures.

In all casting it is difficult, where there is any sudden variation of thickness, to ensure that uneven cooling will not set up stresses or absolute defects, and owing to the plasticity of the aluminium during cooling it is very apt to be pulled apart at the junction of a thicker portion of the casting with a thinner part, and this is overcome by the scientific placing of "chills" in the mold on the face of a thick portion. In other words, heat reduction is accelerated in the thick portion, so that it and the thin portion may cool approximately at the same rate—another proof, if proof be required, that there is no little similarity between the processes of geology and those of the foundry.

The alloying of metals is one of the most complicated chemical processes, because all sorts of things which are unexpected to the layman are encountered. For instance, pure aluminium melts at a temperature of about 660° C., yet practically all the alloys commonly used rich in aluminium melt at a still lower temperature, though the addition of, say, copper, is the addition of a metal which has a higher melting point than aluminium, and therefore at first sight it would be imagined that the melting point of the alloy would be higher than that of the pure aluminium.

The alloys of aluminium with copper are of particular interest because both in alloys rich in copper and alloys rich in aluminium are found alloys which have properties of great value to the engineer—those with a low percentage of aluminium are nearly uncorrodible by sea water either alone or when attached to steel, and are only slightly corrodible in fresh water. Then at the other end of the series there is the alloy with only 1 per cent to 15 per cent copper and the rest aluminium, which is most valuable for many purposes. The alloys of aluminium, zinc, and copper have very considerable possibilities, and are used to a very large extent, but not so much research work has been conducted in regard to them as in the binary alloys, that is, the various proportions of copper and aluminium.

A number of other alloys were mentioned by Mr. Hill in his paper, but perhaps the most interesting referred to are manganese and magnesium. One and one-half per cent to 2 per cent of manganese with a small percentage of copper up to 4 per cent or 5 per cent, and the rest aluminium, give an alloy with great hardness, and the lecturer mentioned that 0.2 per cent to 0.4 per cent of manganese had been found in the alloys of which the angle and channel sections used in Zeppelin airship construction have been made. He also stated that the well-known Vickers alloy "Duralumin" contained traces of manganese.

Perhaps, however, the greatest indication of future developments came in the reference to magnesium, which has been much advocated as the means of producing a strong light alloy of aluminium. Its very low specific gravity—1.75 to aluminium 2.56—obviously means that the greater the quantity of magnesium added to the aluminium the lighter the resultant alloy becomes. On the other hand, with the majority of aluminium alloys the additional metal increases the weight. Unfortunately at the present time magnesium is rather

difficult to obtain, as well as being expensive, but it has great possibilities which may and probably will be exploited at some later time.

Mr. Hill dealt at some length with aluminium pistons, but in the main he considered facts already well known to our readers, though in regard to the aluminium alloy piston he brought up the interesting fact that the tensile strength of copper alloys falls rapidly as the temperature rises, and it is therefore clear that the heat conductivity of aluminium is a very real help to the piston itself in a way not usually borne in mind. It was pointed out, however, that the ideal is to find an alloy which, while maintaining all the other advantages of an aluminium alloy, would also have the property that its tensile strength up to a certain degree would rise with the rise in temperature; such an alloy has indeed been discovered, but experiments are only in progress, and nothing more could be said about this. It will be realized that it is of the very greatest importance, because it follows necessarily that if an alloy in which rise in temperature increases strength can be successfully used, it is obvious that with the same margin of safety a still lighter piston can be used.

With regard to the working of aluminium pistons, Mr. Hill pointed out that they have been used most successfully with steel and cast iron cylinders, but on the whole better results were obtained in working aluminium against cast iron, as then, under suitable conditions, it was found that the walls assumed after long running just the same beautiful glaze as they do with cast iron pistons, and the wear was no greater than with cast iron.

Another interesting branch of the paper was in regard to die casting. Motorists hear a good deal about it nowadays, and they, in common with a good many engineers, are very hazy in their minds as to what it means, and we cannot do better than give the author's classification of the three distinct classes of the process, which are: (1) Casting under pressure into a mold which is entirely of metal (instead of the usual sand in which, of course, pressure could not be introduced); (2) casting without pressure into an entirely metal mold; (3) casting into a metal mold some small part of which such as a core, is of sand, because the nature of the casting is such that it could not be arranged in any other way.

The advantages of die casting are rapid production, accurate and uniform dimensions in the castings, thus reducing machining; a closer grain; increased strength in the metal in some cases; and last but not least an improved finish in the casting. So far as the motor car is concerned, die castings have been mainly employed for details such as magneto parts, electrical installation fittings and so on, but they can be used for crank cases, gear boxes, and other large parts.—*The Autocar*.

A Material for Ships' Propellers

An alloy that has proven very satisfactory for ships' propellers, is turbadium bronze. This material has a tensile strength of 35-42 tons with an elongation of 14-20 per cent on a two-inch test piece, and it is not appreciably corroded by sea water. According to the *Chemical News* its composition is, approximately, copper 48 per cent; zinc 46, 45; tin 0.5; lead, 0.1; iron 1; aluminium 0.2; manganese 1.75; nickel 2.