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3,097,090

METALLURGICAL PROCESS

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This invention relates to metallurgy in general and more particularly to processes for the calcining and prereduction of metallurgical ores. More particularly, the invention involves the provision of an improved process whereby a high degree of pre-reduction of metallurgical ores may be obtained without adverse effects on equipment or the ultimate carbon content of end-product metal produced upon subsequent smelting of the partially reduced charge.

In the pre-treatment of metallurgical ores prior to smelting, the rotary kiln is a highly advantageous device. It is the purpose of the kiln, variously, to dry and calcine the ore, to sinter and agglomerate fines, to oxidize arsenic and sulfur, to burn volatiles from admixed coal, and to reduce the contained oxides, partially, to metallic form. It was realized at an early date that in order to perform the latter function—metallization of the oxides—it was necessary to add carbonaceous reductant in excess of that required for the actual reduction of the oxides. While this presents no particular problem to the kiln operator, the excess carbon normally carried over in the kiln discharge is not conducive to proper furnace operation. It was postulated as early as 1927 that if the excess carbon could be separated from the kiln discharge, the kiln could be run at a high rate of metallization and subsequent furnacing steps would not be impaired. While this proposition is simple enough, practical means for carrying it out have proved elusive.

One solution to the problem which has reached the stage of semi-commercial operation is to pass the kiln discharge containing excess coke through a rotary cooler, followed by fine-grinding of the cooled product in ball mills, ultimately separating the reduced iron, in sponge form, from the residual reductant by magnetic separation practices. While this accomplishes the desired result, it involves a substantial investment in capital equipment and results in a large loss of thermal efficiency due to the necessity for cooling the discharge to effect separation of the metal and carbon.

An alternate process proposal achieves a high degree of prereduction through encouraging intimate contact between finely-divided ore and reductant, rather than depending on a large excess of reductant to "smother" the ore. This is achieved by mixing hot, fine, ore with fine coal at a temperature in the coal's plastic range. Mixing is carried out in a rotary device which causes the ore-coal mixture to pelletize, and the pellets are readily reduced in a subsequent kiln operation. While this process also accomplishes the desired result of high pre-reduction, it has the severe limitation of being workable with only very fine, highly reactive ores—mostly —325 mesh. This fills a need, as such ores cannot be used in a conventional blast furnace, but the energy of comminution required to make conventional lump ores amenable to the process is very high.

The present invention is based on detailed study of both chemical reactions within a rotating kiln, as well as kinetic factors present in the treatment of oxidic ores in a rotary kiln. Considering that reduction of a particle of ore must proceed from the outside of a particle toward the inside, it is logical to expect that reduction will be greatest for particles having the highest surface-to-volume ratio; that is, for the smallest particles. Experimental evidence, however, shows that this is not so. Table I pre-

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sents results of a typical ore, in which metallization was found to be greatest in intermediate sized ore particles—those about the size of a grain of wheat.

TABLE I.—REDUCTION IN KILN

Screen size of ore:	Percent of metallization
+3 mesh-----	20.6
+6 mesh-----	27.8
+12 mesh-----	33.34
+28 mesh-----	33.7
—28 mesh-----	11.9

The reason for this phenomenon is believed to be grounded in two facts. The first is that while the atmosphere in the bed of ore and reductant is highly reducing, the atmosphere in the rest of the kiln (over the bed) is oxidizing, being largely carbon dioxide and nitrogen. The second point is that while the very small particles are easiest to reduce, they are also easiest to reoxidize. Thus, as the small particles cling to the side of the kiln as it rotates, which they have a decided tendency to do, they are exposed to an oxidizing atmosphere and will quickly reoxidize. Furthermore, when the small particles leave the kiln and are exposed to air before charging to the furnace, they have a strong tendency to reoxidize.

By studying the behavior of small particles under normal conditions of kiln treatment it was determined that two approaches towards increased total metallization were available; (1) to change the atmosphere in the kiln, or (2) in some manner protect the charge from the kiln atmosphere. The first course of action is that basis of copending application Serial Number 36,026 of Frank C. Senior, filed June 14, 1960. The aforementioned prior processes take the latter course by literally smothering the ore in the reductant through the sheer volumetric addition of reductant to the kiln burden.

The present invention accomplishes the same result by supplying an excess or protective carbon cover in a physical form that effectively and efficiently excludes the oxidizing atmosphere from reaching the ore particles. This is achieved by supplying substantially all of the reductant, in excess over the theoretical quantity required, in the form of lumps substantially larger than the remainder of the charge. Thus, while reducing carbon, ore, and fluxes are all minus ½ inch, the protective carbon may be 1½ inch to fist size. As with any aggregate under conditions of continuous agitation, the small sized ore and carbon particles settle into a dense, close-packed relationship, leaving the large lumps of protective carbon on the bed surface, thereby forming a protective shield from the oxidizing atmosphere.

Perhaps the greatest advantage of using large lumps of protective carbon is the ease with which it may be separated from the rest of the charge prior to introduction of the kiln discharge into the smelting furnace: a simple hot-screening operation, for example, serving to remove all of the lumps over a predetermined size. The hot lumps of protective carbon are immediately recycled to the front-end of the kiln and, along with fresh lumps to make up for reductant consumed in the operation, are added to the ore-reductant charge. In this manner, a substantial thermal economy is effected, as the sensible heat of the protective carbon is fully utilized, and the ore is delivered to the furnace in a highly reduced state, with no chance for reoxidation nor undue contamination of the metal product by reason of the presence of a large excess of reductant.

In operation, the kiln charge is prepared in the conventional fashion, and to it is added sufficient protective carbon, in lump form, to provide an effective cover. The actual amount necessary in any particular instance is determined by the degree of pre-reduction desired and

atmospheric conditions within the kiln. The fact that larger pieces of reductant tend to travel through the kiln at a slightly faster rate than the more finely-divided ore and reductant must also be taken into account. The lumps of reductant may either be mixed with the other charge constituents or added to the kiln simultaneously with the charge; in either case the ore and finely-divided reductant will settle to the bottom within the first few revolutions of the kiln, leaving the lumps as a protective layer on top of the bed. The kiln discharge is an easily-handled, free-flowing product which needs only to be hot-screened to remove the lumps of excess reductant before charging directly to the smelting furnace.

A slightly modified operating technique serves to insure the ultimate production of metal with a very low residual content. In the practice of this modification, an amount of finely-divided carbonaceous reductant sufficient only to pre-reduce the ore to a predetermined degree, for example, fifty (50%) percent, is mixed with the ore. A quantity of carbonaceous reductant in lump form is added as before, but in this case the carbon not only provides an effective cover but also takes an active part in maximizing pre-reduction or metallization, so that all of the finely-divided carbon and some of the lump carbon will be used up in the kiln operation. With a kiln discharge of such composition, the furnace feed, after hot-screening of residual lump carbon, will be essentially carbon free. Thus, reductant can be added to the furnace in the precise stoichiometric amount necessary to complete the metallization of the kiln product, and, at the same time, insure that residual carbon in the metal as tapped will be minimal. Alternatively, the carbon carry-over in the kiln discharge can be deliberately adjusted to the stoichiometric quantity required for total metallization in the smelting furnace.

As an illustration of the inventive novelty of the process of the present invention, reference is made to U.S. Patent 2,684,296, wherein it is taught that to accomplish the objective of high-pre-reduction in a kiln, a cover of fine ore should be placed over the bed. While this will sinter and form a suitable protective layer over the bed, the shortcomings of such a process are obvious: fine ore will not stay on top of the bed under agitation, so kiln cars running through a tunnel furnace or the kiln must be employed. This requires a substantial additional capital investment and would tend to reduce the rate of production. To separate the covering layer from the bed, "slight pressure" is needed to break up the layer, after which it may be screened off and recirculated (cold) as part of the charge. Thus, an extra step of breaking up the cover is necessary, and its sensible heat is lost. It is significant to note that the process described in this patent, so directly contrary to the teachings of the present invention, is not believed to have reached even limited production.

It is to be specifically noted that the process of the present invention can be employed advantageously in conjunction with the processing techniques described and claimed in copending application of Frank C. Senior, Serial Number 36,026, filed June 14, 1960, and with the techniques described and claimed in copending application of the present inventor, Serial Number 38,121, filed June 23, 1960. In the former, a kiln featuring a unique differential oxidizing and reducing zone is described. It is entirely possible to perform the process of the present invention in conjunction with the operation of the reducing zone of said copending application and thereby improve its efficiency. The latter copending application describes a process for increasing the selectivity of carbo-thermic reduction operations by means of adding measured amounts of lump ore to the kiln feed which, when fed to the smelting furnace, sink to the slag-metal interface and serve to selectively oxidize impurities from the metal into the slag. The process of the present invention may be carried on simultaneously with that of my

copending application, provided that the size of the lump ore additions to the kiln feed are not so large as to be screened out with the excess carbon before being charged to the smelting furnace.

It is believed that the process of the present invention may be best understood by consideration of the following specific examples illustrating the application of the foregoing principles and procedures to a typical metallurgical ore:

Example

A Tilden siliceous hematite ore, containing 36.95 percent iron and 42.40 percent silicon, was selected for the trial. On previous runs with this ore, which is finally smelted to a 45-50 percent ferrosilicon, pre-reduction in the rotary kiln averaged 33 percent. The theoretical amount of fixed carbon necessary to reduce the iron contained in the ore amounted to 117 pounds per 1000 pounds of ore. Additional carbon, amounting to an excess of 145 percent over the amount necessary to smelt the iron alone, was also added. The carbon was half in the form of finely-divided soft coal and half as "pea-coke" of 1½ inch size. The latter formed the layer of protective carbon. Results, giving the metallization of each size fraction of the ore, are shown in Table II.

TABLE II.—ANALYSIS OF KILN DISCHARGE

Mesh Size	Percent of Charge	Total Fe, Percent	Metallc Fe, Percent	Percent Pre-reduction Metallc Fe/Total Fe
½ inch	6.61	16.39	7.74	47.2
3	36.35	37.06	26.79	72.3
6	26.72	38.22	27.36	71.4
12	16.09	39.25	29.67	75.6
28	7.47	39.14	28.63	73.2
35	1.72	39.94	28.40	71.2
48	1.44	38.79	29.67	76.4
65	1.44	44.22	34.98	79.1
100	1.00	43.64	34.29	79.7
-100	1.15	28.63	18.94	66.2

The table shows that reduction was substantially evenly distributed over small and large particles, and amounted to over twice the reduction obtained with previous conventional practice. The material was free-flowing in the kiln and did not show any tendency to stick to the kiln walls. The kiln discharge was transferred to an electric furnace in insulated hopper buckets and, as it was charged into the furnace, the large sized coke particles were hot-screened out and recycled to the kiln. Smelting in the furnace was carried out in the established manner with a substantial saving of power, due to the high pre-reduction of the furnace charge. It is emphasized that any suitable carbonaceous material, such as anthracite or pelletized carbon, would form a suitable protective layer and the process is not limited to using coke for this purpose.

Having thus described the subject matter of my invention, what it is desired to secure by Letters Patent is:

1. In a process for the partial pre-reduction of iron oxide-containing materials in a rotary kiln, the improvements that comprise introducing into said kiln a charge of said oxide-containing materials which is substantially within the size range of minus 3 to plus 28 mesh, and finely-divided carbonaceous material, so proportioned as to effect partial pre-reduction of oxides in said kiln while providing sufficient excess residual carbon to bring the discharge from said kiln to total metallization upon subsequent smelting thereof, adding to said kiln charge lumps of carbonaceous material of at least approximately 1½ inch size, said lumps being substantially in excess of the carbon theoretically required in said kiln and serving to promote pre-reduction of said oxides to a higher degree than normally obtainable with said finely-divided carbon alone and also serving to protect said charge from re-oxidation, said lumps being capable of physical separation from the remainder of said charge after discharge from

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said kiln to effect the production of a substantially pre-reduced furnace burden for said subsequent smelting operation which is uncontaminated with excess carbon.

2. In a process for partial pre-reduction of iron oxide-containing materials in a rotary kiln, the improvements that comprise introducing into said kiln a charge of said oxide-containing materials which is substantially within the size range of minus 3 to plus 28 mesh, and finely-divided carbonaceous material, so proportioned as to effect partial pre-reduction of said oxide materials and total consumption of said finely-divided carbonaceous material within said kiln, adding to said kiln charge lumps of carbonaceous material of at least approximately 1½ inch size to promote pre-reduction of said oxide materials within said kiln to a high degree and prevent re-oxidation thereof, said lumps being capable of physical separation from the remainder of said charge after removal from said kiln to effect the production of a partially reduced, substantially carbon-free furnace burden which, upon the subsequent addition of the precise stoichiometric amount of carbon required to complete reduction in said furnace, will yield a substantially carbon-free metallic product from said furnace.

3. A process for partial pre-reduction of iron oxide-

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containing materials in a rotary kiln that comprises introducing into said kiln said oxide material substantially within the size range of minus 3 to plus 28 mesh in admixture with a finely-divided carbonaceous reductant, and substantially larger pieces of additional carbonaceous reductant of at least approximately 1½ inch size, said finely-divided reductant being present in an amount sufficient to reduce said metallic oxides at least in part to the metallic state and said larger pieces of reductant being present in an amount sufficient to form an effective cover over said kiln charge, establishing a moving bed of said charge and carbonaceous cover within said kiln at an elevated temperature to effect at least partial reduction of said oxides, and discharging said charge and carbonaceous cover from said kiln.

4. The process as claimed in claim 3, wherein said larger pieces of reductant are removed from said charge after discharge from said kiln, and are recycled to the charge end of said kiln.

References Cited in the file of this patent

FOREIGN PATENTS

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