July 18, 1939. W. E. GREENAWALT 2,166,759

METALLURGICAL PROCESS

Filed Jan. 23, 1937 2 Sheets-Sheet 1

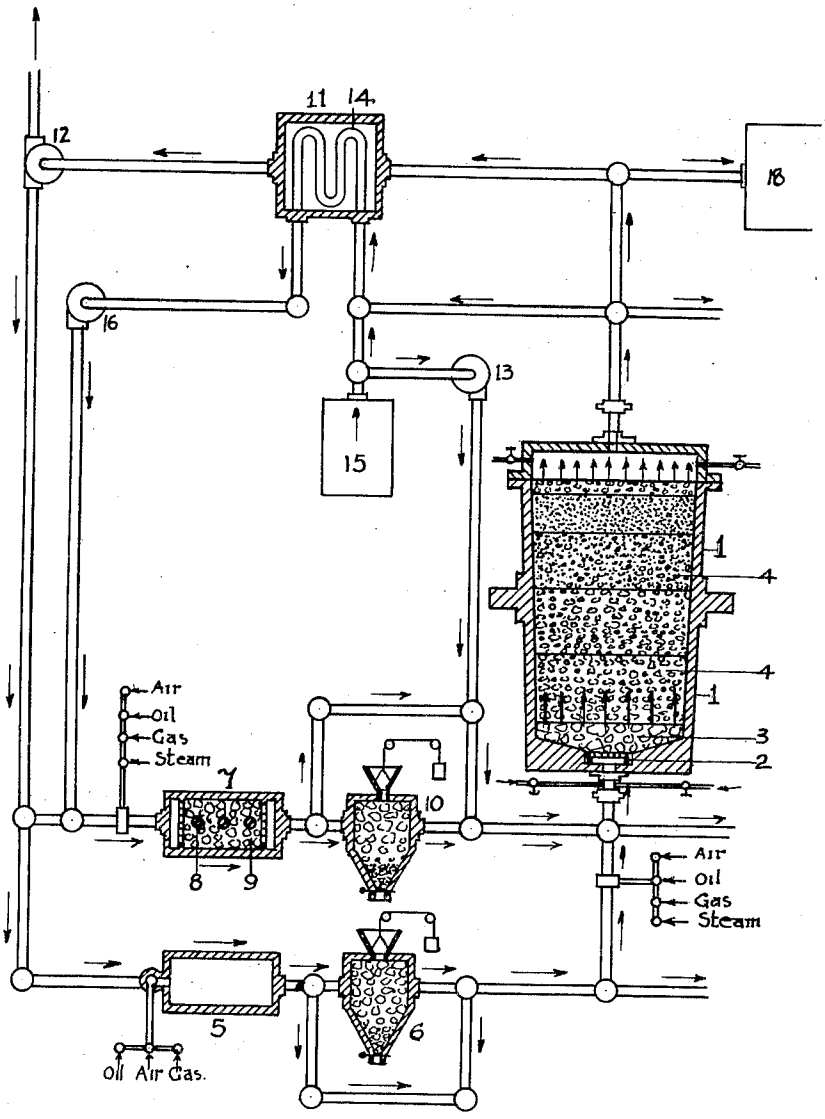


FIG 1

INVENTOR.

William E. Greenawalt.

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METALLURGICAL PROCESS

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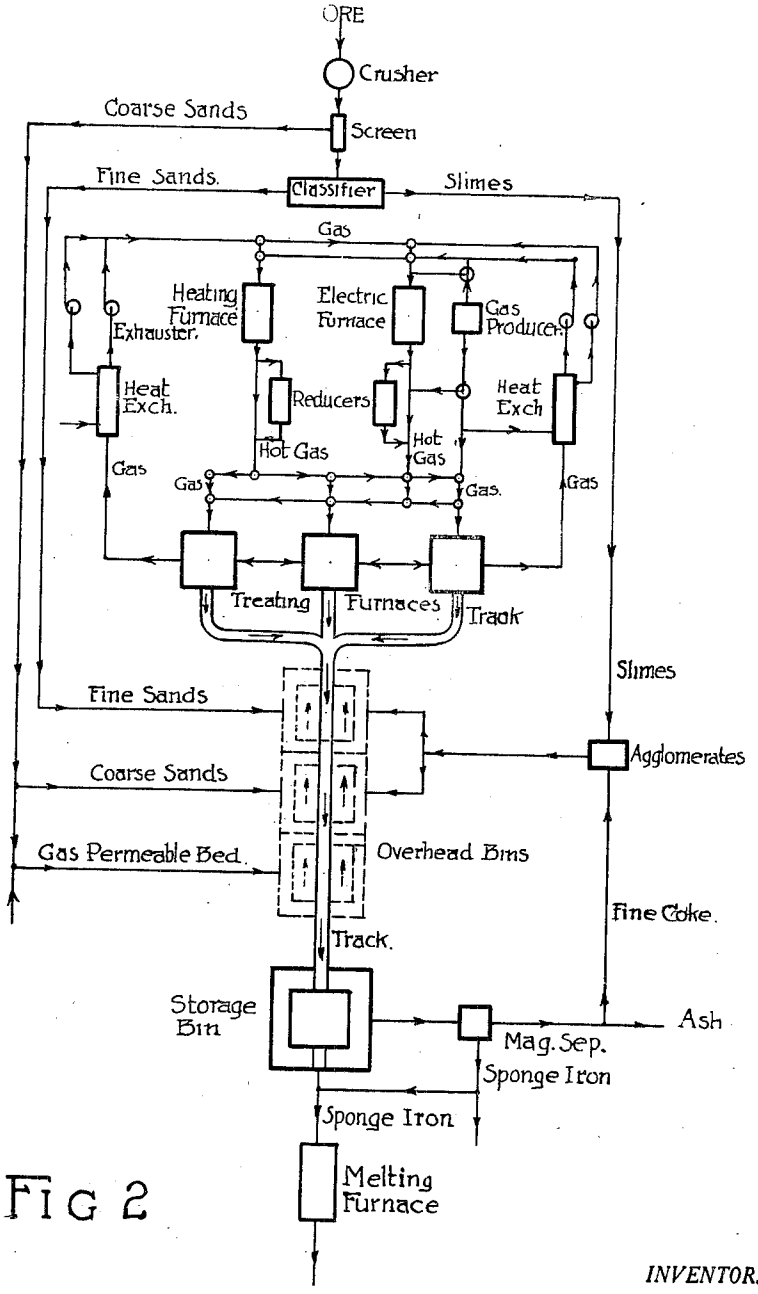


FIG 2

INVENTOR.

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Patented July 18, 1939 2,166,759

UNITED STATES PATENT OFFICE

2,166,759

METALLURGICAL PROCESS

William E. Greenawalt, Denver, Colo.

Application January 23, 1937, Serial No. 121,999

13 Claims. (Cl. 75—91)

My invention relates to metallurgical processes. It has wide application, but it will be described more particularly in connection with the treatment of iron ore to produce sponge iron; to the treatment of zinc ores to produce metallic zinc; and to the treatment of sulphide ores to produce elemental sulphur. In all of these and similar processes it is necessary to closely control the temperature, the condition of the reacting gases, and the time of treatment.

The object of the invention, in general, is to make practical, especially on a large scale, the reactions between ore and a highly heated reacting gas without externally heating the treating furnace, or retort, and without disturbing the ore during treatment. Its more immediate object is the reduction of oxidized ore, such as the oxides of zinc and iron to produce metallic zinc or sponge iron, which require a high temperature, usually about 900 to 1100 deg. C. only (1652 to 2012 deg. F.); such temperatures are impractical of attainment in the interior of large externally heated furnaces or retorts, and agitation or movement of the ore under such temperatures is so highly destructive of the agitating or moving mechanism as to become operatively impractical. A further object of the invention is to percolate a highly heated gas uniformly through a stationary mass of ore under condition of uniform temperature throughout the mass.

The details of the apparatus may vary to conform with the particular material to be treated, but in general the apparatus will be constituted as shown in the accompanying drawings, in which Fig. 1 is a vertical section, and Fig. 2 a flow sheet in horizontal plan of the process and accessories as it is preferred to carry it out in more or less continuous operation.

Referring to the drawings, 1 is a treating furnace, rotatably mounted, containing the material to be treated. It has a gas inlet at the bottom, and a gas outlet at the top, preferably in a removable cover, which is closely fitted to the body of the treating furnace to prevent leakage of gas either inwardly or outwardly, although it need not be absolutely air tight. At the bottom of the furnace, covering the gas inlet, is a grate 2, usually made of a high heat resisting alloy, and loosely fitted, so that it can be dumped with the charge when the treating furnace is rotated to empty it. Over the grate, and supporting the charge, is a gas permeable bed 3 of loose material which has been crushed to a convenient size and from which the fines have been removed to permit the free distribution of the gas through the bed, so that the gas can be percolated or blasted evenly through the charge 4.

The treating furnace will ordinarily be constructed of a shell of cast or sheet steel, lined on the inside with refractory heat-resisting metallic cast plates bolted to the shell, and backed with a refractory heat insulating cement. The treating furnace may be as large as convenient for practical operation. There need not be any metallurgical limit to the size of the furnaces: the size limit will be constructional. A small furnace having effective charge dimensions of 6 x 6 x 8 feet would have a capacity of about 15 tons per charge: a medium size furnace having effective charge dimensions of 8 x 8 x 13 feet would have a capacity of about 40 tons: a large furnace 12 x 12 x 15 feet would have a capacity of about 100 tons per charge. With such capacities an intermittent process presents marked advantages over a continuous process.

5 is a heating furnace, preferably fired with oil or gas, to avoid dust or ash, which may have a tendency to clog the charge in the treating furnace or the pipes leading to the treating furnace. The hot products of combustion are piped directly to the treating furnace and percolated, or blasted, through the charge to heat it and to bring it to a reacting temperature. If it is necessary or desirable to rectify, or reduce, the gaseous products of combustion from the heating furnace 5 before passing them through the charge in the treating furnace, they may be passed through the reducer, or reactor, 6, containing coke or other reacting material.

7 is an electric furnace for heating the reacting gas to the necessary temperature, after the charge has been brought to about the reacting temperature with the heated gas from the electric furnace 5. The electric furnace is preferably constructed of a steel shell, reasonably tight to prevent the leakage of gas either inwardly or outwardly, and lined on the inside with a highly refractory heat-insulating material, such as magnesite. Within the furnace are electric resistors 8 of known properties embedded in, or surrounded by, a gas-permeable mass of highly refractory material 9, such as pieces of magnesite, which are practically unaffected by high temperatures or by the highly heated gas. Non-metallic resistors, such as globar, have a working temperature range up to 2750 deg. F. (1510 deg. C.) and unit capacities up to 50,000 watts. With large resistor units in the electric furnace it be-

comes practical to have a simple arrangement between the electric conductors on the outside of the furnace and the highly heated resistors on the inside to permit of a small pressure of gas inwardly or outwardly without appreciable leakage of gas. The gas permeable mass of highly heated material surrounding the resistors offers a large heating surface with a relatively small furnace. The conditions of the electric furnace, once adjusted, will remain practically constant, and will at all times be under delicate control.

10 is a reducer, usually a carburetter, to reduce, or rectify, the highly heated gas from the electric furnace before introducing it into the charge in the treating furnace. The reducer will ordinarily be filled with coke, from which the fines have been removed, heated to a high temperature by the gas from the electric furnace. Any reacting fluid, such as oil, steam, air or other gas, may be added at the reducer, at the electric furnace, or anywhere in the system, depending on the process to be carried out and the results desired. If, for example, steam or oil are to be added to the circulating or reacting gas, they may be added at the electric furnace, at the reducer, or at the gas inlet to the treating furnace.

11 is a heat interchanger communicating at its inlet with the top of the treating furnace and at its outlet with an exhauster **12**. The gas from the exhauster may be wasted or circulated through the system. **18** is a similar interchanger for use when several treating furnaces are in operation at the same time. **14** is a heater pipe, passing through the heat interchanger and communicating at its inlet with the top of the treating furnace **1** or with a gas producer **15**, which produces the gas necessary for the particular reactions desired, and communicating at its outlet with an exhauster-blower **16**, which exhausts the gas from the treating furnace or from the gas producer and delivers it to the electric furnace or to the heating furnace. If relatively cool gas from the producer **15** is to be passed through the ore in the treating furnace without superheating the gas, as for the purpose of cooling the highly heated ore in a reducing atmosphere, the gas may be exhausted from the producer and passed through the charge by means of the blower **13**. Pipes and valves necessary to carry out the details of the treatment of any particular material need not be given special description.

It is practical, especially on a large scale, to design an exhauster which will produce a suction of from 40 to 60 inches of water, or from 1.5 to 2.0 pounds per square inch, which is quite sufficient to suck the gas through the treating furnace and through the heating and electric furnaces with their respective reducers, at a fairly high temperature, or at from 500 to 1500 deg. F. (260 to 816 deg. C.) especially under the conditions of operation of this process, which in most instances contemplates the removal of the slimes, or extreme fines, from the charge, thus removing the greatest resistance to the flow of gas through the charge.

Iron ore reduction.—The operation of the process will now be described as applied to the reduction of iron ore to produce sponge iron, using carbonaceous fuel as a reducing agent.

The ore is crushed to a suitable size, ranging, ordinarily, from several inches to one-fourth inch, depending upon the nature of the ore. One inch will probably be a good average. The extreme fines, or slimes, are preferably separated from the coarse ore, or sands, and the sands are preferably classified, either wet or dry, into several sizes. The slimes will usually represent the fines which would seriously impede the rate of flow of gas through the sands, which may vary somewhat with the nature of the ore and the details of the metallurgical treatment. The largest size for the sands will usually range from one-fourth to one inch. The coal, or preferably hard coke, is similarly crushed and classified. The corresponding sizes of ore or of ore and coke, will usually be mixed to give uniformity for gas flow. The classified sands may be assumed as one inch, one-half inch, one-fourth inch, one-eighth inch, and finally the finer sands with the slimes removed. If the ore is a concentrate, the charge will ordinarily be classified into coarse and fine sands, with the slimes taken out. A layer of coarse ore, coke, or inert refractory material, is placed upon the grate to form a gas permeable support for the charge. If the ore is coarse, this gas permeable bed, or support, may be the coarser ore or coke. The different sizes of sands are charged successively in layers, the coarser sands at the bottom and the deslimed finer sands at the top. A restraining layer of coarse coal or coke may be used to cover the charge to prevent possible oxidation or to prevent fine sands from being drawn out with the gas passing through the charge. The cover is then secured and the exhauster started.

The classification of the deslimed material, or sands, of the charge, while not necessary, is desirable, because it offers the least resistance to the passage of gas through the charge, the gas is very much more equally distributed through the charge, and the coarser ore at the bottom gets the greatest heat and the longest time of treatment, while the smaller sands at the top get the lowest heat and the shortest time of treatment. A layer of 8 mesh or even considerably finer deslimed sands offers no particular resistance to the passage of gas, whereas coarse particles of ore embedded in the finer sands would actually offer more resistance to the passage of gas than the classified fine sands alone. By charging the sands in layers as described the only substantial resistance to the passage of the gas through the charge is in the top layer of fine deslimed sands, and the classification between sands and slimes can be made to conform with any desired or necessary condition of gas percolation through the charge. A little experimenting will determine the sizes necessary so that the time of treatment will be the same for all.

The treatment of the charge may be conveniently divided into three steps, either as carried out in the same treating furnace, or as applied successively to several treating furnaces. First: heating the charge. The hot products of combustion from the heating furnace are passed through the charge in the treating furnace until the charge is brought to the reacting temperature at the bottom and close to the reacting temperature at the top. This temperature will ordinarily be about 800 deg. C. (1472 deg. F.). Combustible waste gases from previous operations may be used in the heating furnace in connection with other fuel. The composition of the heating gas will usually not make any difference, but when the temperature approaches that of reaction, it may be desirable to pass the heating gas through the reducer **6** before it enters the treating furnace, and thus the heating action of the charge may

advantageously be carried to the reacting temperature, thus saving the coke in the charge and the more expensive electric heat. The principal object in heating would be to bring the charge as quickly as possible or practical to the reacting temperature by means of the cheapest heat and gas, and carry the heating as far as practical, before applying the electric heat and the reducing gas to carry out the reactions or to complete them if they have been started. If the ore contains injurious volatile elements, such as water and sulphur, they may be almost completely removed in the heating stage, before the reducing action commences. The gas from the heating furnace introduced into the treating furnace at the bottom, is at once evenly distributed through the gas permeable bed, or support, and will rise evenly through the charge, and thus the entire charge is quickly and evenly heated with the utmost economy of fuel, no matter how large the treating furnace may be. The principal resistance to the passage of the gas will be in the layer of the finer sands at the top, but since this layer is usually quite shallow and free from slimes the circulation of the gas may be controlled as desired. The products of combustion from the heating furnace will contain the carbon almost entirely in the form of carbon dioxide, and carbon dioxide is not appreciably reduced to carbon monoxide below 800 deg. C. (1472 deg. F.) by coke, so that the charge may be heated to at least that temperature, and perhaps higher, without reacting with the coke in the charge. Second: treating the charge. When the charge has been brought to about the reacting temperature, the valve in the pipe from the heating furnace is closed and the one in the pipe from the electric furnace is opened. Carbon monoxide, coal gas, water gas, natural gas, or any other suitable gaseous reducing agent is passed through the electric furnace and heated to the necessary temperature to assure a temperature of from 850 to 1000 deg. C. (1562 to 1832 deg. F.) in the charge in the treating furnace. The reducing gas, coming in contact with the highly heated coke in the reducer 10 or in the treating furnace 1, is completely reduced, and the gas in the treating furnace, at that temperature, is reduced about as fast as formed by the oxygen liberated from the iron oxide ore. The fact that the temperature and flow of gas may be closely regulated, always assures the best working conditions. Circulating the gas has much the same effect as agitating the ore. Stationary gas and stationary ore does not usually give good results under any conditions. Since a comparatively small amount of carbon dioxide in the reducing gas greatly impairs its efficiency, the effective circulation of the gas, made practical by the removal of the slimes from the ore and the high suction of the exhauster, not only assures the reduction of the carbon dioxide about as fast as formed, but it also assures a uniform temperature and treatment throughout the charge. The gas is circulated through the system principally by means of the suction produced by the exhausters communicating with the top of the treating furnace, and this suction may be varied as desired up to about 60 inches of water. During the second, or reducing, stage of the process, the volume of gas circulated will be relatively small as compared with the first, or heating, stage, because the circulation will be limited to maintaining the necessary or desired temperature, and to that necessary or desirable to most effectively reduce carbon dioxide to carbon monoxide, and to get the most effective time of reduction, which will depend on the temperature, the effective reduction of the carbon dioxide formed by the reactions, and the displacement of the gas in contact with the ore to make the reactions most efficient. All of these factors will have to be determined experimentally for various ores. There are three advantages in classifying the ore and charging the classified sands in separate layers in the treating furnace: (1) it permits free and even distribution of the gas and the heat through the charge; (2) the largest pieces of ore at the bottom have the greatest amount of heat and the most effective gas; (3) the time of treatment is longest for the larger pieces and shortest for the finer sands. Third: cooling the charge. When the reduction is completed, or practically completed, the electric current is shut off from the electric furnace and cold reducing gas, preferably under a slight pressure, is introduced into the treating furnace. If it is desired to complete the reactions, the gas may for a time be kept at a reacting temperature, if advantageous under a slight pressure, in contact with the charge, at no additional expense. But whether this is desirable or not, when the reaction is completed the cold reducing gas is flowed through the charge to cool it below the reacting temperature, while, at the same time, the gas is at first highly heated, and this highly heated gas, after being further heated in the electric furnace, is used as the reducing gas on a new preheated charge. The charge may be cooled to any extent desired after the temperature has been lowered below that of re-oxidation, and the heated air or gas may be used in the heating furnace in connection with atomized oil or other fuel in preheating a new charge to the reacting temperature.

When the charge is cooled sufficiently the treating furnace is rotated on its trunnions and dumped, usually into a bin to be fed out for further treatment, such as magnetic separation. The gas permeable bed is dumped with the charge, and may be separated from the charge and returned to the treating furnace for a new charge. Similarly, the grate supporting the permeable bed may be dumped with the charge. This obviates the necessity of separately removing the grate, or to enter the hot treating furnace to clean the grate. Every charge starts afresh; there are no cumulative injurious effects.

The daily capacity of the treating furnace should be quite large. The time of reduction of iron oxide to sponge iron may vary from less than an hour to more than a day, depending on how closely any process complies with the best conditions; which are, the right temperature throughout the charge, the degree of gas circulation or ore agitation, the nature of the ore, and the effective reduction of carbon dioxide to carbon monoxide. Heating the charge will usually consume most of the time, but in view of the fact that all of the products of combustion, and hence all of the heat, from the heating furnace are passed through the charge in the treating furnace, the time of heating should not be over one or two hours. The time of reduction should not be longer, and the time of cooling may be made quite short, if desired, because sponge iron will not reoxidize appreciably at temperatures below 500 to 700 deg. C. (932 to 1292 deg. F.) in dry air and especially in the presence of carbon. Nevertheless it will usually be desirable to cool to a lower temperature to get hot air or gas for use in other charges. From six to eight hours

might be considered a fair average for a complete cycle of treatment. If the iron sponge is to be melted at once, it may be dumped at any temperature directly from the treating furnace into the melting furnace. Or, if it is to be subject to magnetic separation, it can be dumped at any temperature into cooling bins especially designed for the purpose.

The production of sponge iron from its oxide ores has been frequently proposed and a great deal of work has been done to evolve a satisfactory practical process capable of application on a large scale, but apparently, so far, without the hoped for success, although, theoretically the process appears quite simple. The principal lines of approach have been through externally heated retorts, or by heating a moving charge by internal heat, as in a rotary furnace or vertical shaft furnace.

It is quite impractical to heat a retort of large size with externally applied heat. The outside of the retort has to be heated excessively to heat any of the interior, and the central part of the charge is brought to a reacting temperature only with the greatest difficulty, by overheating the retort and the charge adjacent to it. It is rarely that an externally heated retort of two feet or over is attempted. If the charge is treated in a rotating cylinder heated by internal combustion, the hottest part of the furnace is the exposed interior lining at the top, which is usually overheated and forms adhesions which have to be removed from time to time, and in addition, the dust is excessive and presents a problem, and neither the ore nor the gas is under satisfactory control. If the charge is passed through a shaft furnace, heated internally or externally, there is always a mixing of the ore, gas channels are unavoidable, and the problem of passing a column of ore through a shaft in a uniform stream still remains to be solved.

In my process the outside of the treating furnace is the coolest, no matter how large the furnace may be, and the steel shell and the alloy lining can be designed to abundantly withstand the highest temperature of the charge. If need be, they can be artificially cooled. The interior of any part of the charge in a small or in a large furnace can be as easily and satisfactorily heated as any other part. By classifying the ore, or by removing the slimes, and treating the quiescent charge on a gas permeable bed, there is always a uniformity which is unattainable with a moving charge of any kind. It is desirable to separately mix the different sizes of the ore before charging them in layers in the treating furnace, especially the smaller sizes. The idea is to get as even a percolation of the gas through the charge as practical, even though it may not be necessary. The number of classifications can best be determined by experiment, or whether classification is needed or not, after the slimes have been removed from the sands.

The process has, so far, been described when the iron ore is mixed with a solid reducing agent, such as coal or coke. If desired these may be omitted from the treating furnace and the reduction made entirely with a reducing gas, such as carbon monoxide, hydrogen, natural gas, water gas or coal gas. The process offers peculiar advantages when gas is used as the reducing agent instead of solid carbon. The space occupied by coal or coke is occupied by ore, and hence more ore can be treated per charge. Heating of the charge may be carried to the full reacting temperature, either with an oxidizing or with a reducing gas. Many iron ores contain sulphur in undesirable amounts, and sulphur can be almost completely eliminated in an oxidizing atmosphere, but not readily in a reducing atmosphere. Zinc is best eliminated with a reducing gas. It is practical, therefore, to heat the charge in an ordinary oxidizing atmosphere to eliminate elements which can be driven off at roasting temperatures, and then follow it up with a reducing gas which will drive off the elements volatile in a reducing atmosphere, leaving behind the relatively pure sponge iron. Reducing gases, such as coal gas and water gas, usually contain small amounts of free oxygen and carbon dioxide. The reducing gas, reacting with the oxygen of the ore, is oxidized, and thus gradually impairs its efficiency as a reducing agent. When carbon is mixed with the ore the reduction of the oxidized elements in the gas is quickly brought about by the carbon mixed with the ore. When, however, there is no carbon reducing agent mixed with the ore, the reduction of the gas must be made outside of the treating furnace, and the gas circulated at such a rate that its reducing action will not be appreciably impaired. This is done by means of the reducer 10 which is always filled with carbon heated to the most effective reacting temperature for the reduction of carbon dioxide to carbon monoxide, or a temperature approximating 900 to over 1000 deg. C. (1652–2732 deg. F.). This active circulation of the gas has much the same effect as agitating the ore, for effective reduction. The reducer 10 is heated by the superheated gas from the electric furnace, and the reducer can be operated without interfering with the electric furnace or with the treating furnace. There is no ash or coke residue to interfere with the even percolation of the hot gas through the charge in the treating furnace, and the hot treated charge, free from foreign matter, may be dumped, without cooling if desired, directly into a melting furnace, or into a heat insulated storage bin supplying the melting furnace, to be fed into the melting furnace as desired.

Under such conditions of operation the cold charge can be brought to the reacting temperature with any cheap fuel, and it can be dumped at about the same temperature for melting, so that about the only electric heat necessary is that of maintaining the reacting temperature in the treating furnace. If carbon monoxide is used largely as the reducing gas, the reactions in the treating furnace will be exothermic, and the electrical heating will be confined mostly to supplying heat to the reducer to convert the resulting carbon dioxide to the monoxide.

Except for dumping, the procass is free from dust. It will usually be desirable to have the treating furnace mounted on wheels, so that, by disconnecting the pipes to and from the treating furnace, the furnace may be shifted for dumping into a specially prepared bin or into a melting furnace, and as it is shifted back to recharge it with the different layers of materials from overhead bins. By having a number of the treating furnaces so arranged, the process may be made practically continuous except for the dumping and charging.

Since the temperature of the interior of the treating furnace is practically under complete control there will be very little danger of fusing the charge, but even if slight fusion occurs it will not in any way interfere with the apparatus or with the effective operation of the process.

Fused lumps will be discharged as easily as the unfused sands.

If the process is operated with three or more treating furnaces, the general procedure would be to heat the first charge with any cheap gas or liquid fuel, using the hot dilute or vitiated reducing gas from a previous charge, in part, as a combustible, and wasting the gas after it has passed through the charge, but with an interchange of heat when the gas is hot. The reducing gas is then applied to the first charge, and when the charge is reduced or nearly reduced, passing the hot reducing gas from the first charge through the preheated second charge. When the reduction of the first charge is completed, the vitiated and cooling gas is passed to the third charge to heat it, as described for the first charge. One charge will be heating, while another is being reduced, and another is being cooled, and perhaps a fourth treating furnace is being dumped and recharged.

The flow of gas through the system is mostly produced by suction. This has the advantage that the hot gases, as hot as 1000 deg. C. (1832 deg. F.), or hotter, may be passed through the system without intervening mechanism between the heating and electric furnaces and the treating furnace. Similarly, it would be impractical to pass the hot gas through the system by pressure exerted at the heating or electric furnaces gas inlets, with ordinary atmospheric suction at the outlet of the treating furnace or heat interchanger.

The resistor in the electric furnace is preferably embedded in a gas permeable mass of neutral refractory material, rather than a reacting material, such as coke, because if a neutral refractory is used, the electric furnace will be operated under reasonably constant conditions and will require little attention, whereas if a reacting material is used, such as coke, ash will accumulate, the coke will have to be changed, the electric furnace may lose its efficiency and give a lot of trouble, and might at any time become inoperative. If the gas is passed through a mass of inert refractory material in the electric furnace to superheat it, and then through a mass of coke, the electric furnace will operate reliably, the reactions will be confined to the coke in the reducer, and the reducer can be designed so that it may be charged with coke and the ashes removed from below the charge without inflow or outflow of either air or reducing gas.

A recuperative furnace may be used for heating the reacting gas, instead of an electric furnace, but a recuperative furnace is not under the same delicate control as an electric furnace, and, since the electrically heated gas is confined to supplying the heat consumed by the reactions in the treating furnace, it can be maintained at relatively small expense.

The division between sands and slimes is determined for each particular material and condition. Ordinarily it will be determined by the rate of flow of gas desired through the charge in the treating furnace. Wherever the division is made, the slimes, or particles so fine as to retard the desired flow of gas through the charge, usually have to be treated. This may be done by agglomerating the slimes by any of the usual methods, such as sintering or briqueting. In sintering the slimes, the resulting sinter is in the form of porous lumps which may be crushed to the desired size for reduction treatment in the treating furnace, with the extreme fines, or slimes, removed, and added to another sinter charge. In this way the charge in the treating furnace may be regulated as desired. If the fines or slimes are briqueted, finely divided coal or coke, such as that obtained by separating the fines or slimes from the coarse coke used in other steps of the process, is mixed with the ore slimes, and pressed, or otherwise formed into agglomerates. These agglomerates are easily reduced; under the right conditions 99 per cent of the iron in the oxide can be reduced in one hour. The unsintered agglomerates may be treated as separate charges, but ordinarily they will form the top layer of a regular charge. In either case there is an advantage in treating the unfused agglomerates by my process, because unfused agglomerates are usually quite fragile, and while they will stand up well if stationary in the presence of moving gas, they will usually disintegrate rapidly under condition of heat and movement. If appreciable disintegration occurs, satisfactory reduction becomes quite impractical.

In classifying the ore into sands and slimes the coarser sizes can be cheaply separated by rough screening. It is preferred to separate the finer sands from the slimes by wet classification because the division can be accurately adjusted and the sands will be clean; this will permit of better penetration of the hot reacting gas into the ore particles and little or no dust will be formed during the treatment. If the ore is a concentrate the separation between sands and slimes may be made wet in the ordinary process of concentration. The flow of gas through the highly heated charge in the treating furnace is greatly facilitated by clean sands and conditions can be so adjusted that there is little or no ash formed during the treatment. The amount of hot gas that can be passed through a layer of clean highly heated sand, even if fine, is surprisingly large.

The same general procedure is used in reducing hematite or limonite to magnetite for concentration by magnetic separation, except that the temperatures may be lower. The conversion of hematite to magnetite, for magnetic separation, will usually be confined to low grade ores. The slimes, removed from the sands, are preferably treated separately, as for example, showering them through a shaft furnace in a reducing atmosphere, as described in my co-pending application, Serial No. 99,192, September 3, 1936.

Zinc oxide reduction.—The procedure is much the same for the reduction of zinc oxide as for iron oxide, except that the metallic zinc is volatilized and is recovered either as metallic zinc or as zinc oxide.

Zinc ore, as treated for the recovery of zinc, is usually in the form of concentrate, and the concentrate is mostly produced by flotation in separating the zinc from other associated minerals. The zinc concentrate is ordinarily in the form of zinc sulphide, which is usually roasted to the oxide before subjecting the ore to reduction to volatilize the zinc. The oxide is treated to form agglomerates, either as sinter, briquettes, or otherwise. The oxidizing roasting can be so conducted that the roasted product will be largely in the form of sinter, which, when the extreme fines, or slimes, are removed, produces an excellent product for the recovery of the zinc by my process. In briqueting, the fine zinc oxide is usually mixed with fine carbon and compressed so that the briquettes will not easily disintegrate under the action of heat. Briquettes will not ordinarily stand up well under the combined action of heat and motion. If the briquettes are stationary during treatment, as in

my process, the disintegration is reduced to a minimum, and there will always be a free flow of gas through the charge of any reasonable size of treating furnace, such as those specifically referred to.

The zinc ore, as coarse and fine sands, with the slimes removed, is charged into the treating furnace, preferably on a gas permeable bed of inert refractory material, or hard coke. The charge may be mixed with coal or coke, or the reduction of the coarse ore, or sinter, may be done entirely with a reducing gas, such as coal gas, water gas, natural gas, or vaporized oil.

The charge is first heated by passing the highly heated gas from the heating furnace through it. This heating gas will usually be the hot products of combustion of any gaseous or liquid fuel, and, as in ordinary roasting, the atmosphere is usually oxidizing. The charge may be heated in an oxidizing or in a neutral atmosphere until it reaches a temperature of from 900 to 1000 deg. C. (1652 to 1832 deg. F.), at which temperature a large part of the impurities of zinc ore, such as sulphur, lead, arsenic, cadmium, are, or may be, volatilized. When the charge has been heated to the desired temperature and the elements volatile in a highly heated oxidizing atmosphere have been removed to the desired extent, the heating furnace is shut off and the highly heated reducing gas applied to the ore. The reducing gas is most effective at a temperature of about 1400 deg. C. (2552 deg. F.) or at as high a temperature as the charge will stand without excessive sintering or slagging. The permissible amount of sintering will be principally limited by its effect on the volatilization of the zinc, because, dumping of the charge is in no way effected by sintering or partial fusion, and the cooled or the hot uncooled charge can be dumped without any part of it adhering to the treating furnace. If the zinc residues contain gold, silver, or copper, as they frequently do, the hot residues may be charged directly into a smelting furnace or into a heat insulated storage bin from which it can be drawn into a smelting furnace.

If the zinc is reasonably pure, the concentration need not be carried to fine grinding, and the particles may be reasonably coarse; in which case the slimes, or extreme fines which would interfere with the reasonably free flow of gas through the hot charge, would be removed from the sands and sintered or briquetted. The briquettes are usually placed on top of the regular charge of sands in the treating furnace; so placed, they are free from undue crushing strains, either of weight or motion.

Production of elemental sulphur from sulphides.—In operating the process for the production of elemental sulphur from sulphide ore, the ore is, preferably, crushed to ¾ inch, and screened to ¾ inch, 2 mesh, 4 mesh, and 8 mesh sizes to remove the coarser sands. The finer ore, passing through an 8 mesh screen, is, preferably, subjected to wet classification, which is best adapted to separate the fine sands from the slimes. The distinction between sands and slimes will be determined by the rate of flow of gas desired or necessary through the charge in the treating furnace. The number of classifications will also be determined by experience—the fewer the better, with the same results. In the treatment of ordinary sulphide concentrate, the classification into coarse and fine sands with the slimes eliminated, will ordinarily be sufficient.

A layer of ¾ inch size is first placed upon the grate or on the gas permeable support, or bed, followed by the various sizes of coarse sands with the fine deslimed fine sands on stop. The gas permeable bed may be either of inert material, but, preferably, the coarser sulphide sands, which, while subject to treatment, will also serve to support the finer sands above it, and permit of a free horizontal distribution of the gas in the lower part of the treating furnace previous to its percolation upwardly through the charge.

The charge is first heated to about 600 deg. F. (310 deg C.) or to a temperature just below the volatilization of an appreciable amount of sulphur from the ore. This heating is preferably done by burning the cheapest fuel available, in the heating furnace, and passing the hot gaseous products of combustion through the charge. Gaseous fuel is preferred to avoid ash accumulation in the charge. Heated air or other gas from a previous charge may be used in the heating furnace. The exhauster will cause the necessary flow of hot gas or of products of combustion through the ore charge.

After the charge has been brought to the reacting temperature, highly heated gaseous reducing fluid, such as natural gas, water gas, coal gas, or atomized oil, to which may be added steam, is passed through the charge of hot ore. The temperature of the reducing fluid will ordinarily be between 700 and 950 deg. C. (1292 to 1742 deg. F.) or just below or just above the fusing point of the ore charge. If the treated charge residue is to be smelted for the recovery of contained metals, the fusion may, in the later stages, be carried to sintering. The gaseous fluid may be brought to the stipulated temperature by incompletely burning oil or gas in the heating furnace or in the lower part of the charge in the treating furnace, but where electricity is reasonably cheap, the gas or the atomized oil is best brought to the necessary temperature in the electric furnace, because its reducing action is unimpaired and the temperature can be accurately controlled. Only sufficient oxygen should be introduced with the gas to supply the reactions, and this will ordinarily be supplied by the gas itself or through the water vapor introduced with the gas. The gas and steam may be so controlled that practically all of the sulphur will be volatilized in elemental form. Air, reducing gas, oil, or steam may be introduced directly into the treating furnace through pipes at or near the gas inlets to the furnace. Their amounts can readily be regulated by valves to give the desired results as determined, principally, by the nature of the escaping fumes above the charge.

Referring to Fig. 2, which represents a flow sheet of the general preferred method of operation with a number of treating furnaces: The ore, as mined, is crushed to the desired size, as determined by experiment. The crushed and ground ore may be concentrated. In either case, the ore is passed over coarse screens to classify the coarser sands. The remaining fine ore is then delivered to a wet classifier, where the fine sands are separated from the slimes. The sands may be of any or all suitable sizes for the process, with the slimes removed. The slimes may be any fines which on experiment would be found to retard the desired flow of gas through the deslimed sands. If coal or coke is mixed with the ore, it may be similarly crushed and classified, and the corresponding sizes of ore and carbon mixed. The classified sands are placed in storage bins. The slimes are usually mixed with the correspondingly fine carbon and agglomerated, either as sinter, briquettes, or otherwise.

The flow sheet shows four treating furnaces mounted on tracks; three in treating position and a fourth in dumping position. The first furnace is assumed to be under heating, the second under reaction; the third under cooling, or under digesting, if the charge is to be cooled, or if it is to be given a slow finishing heat treatment. In either case, the finished charge, represented by the fourth treating furnace, is in dumping position, where the charge, usually including the metal grate, and gas permeable bed whether composed of coarse ore or some other material, is dumped through a suitable grate either directly into the melting furnace or into a heat insulated storage bin if the ore is hot, to be drawn into the melting furnace as desired. If the ore is to be magnetically treated, the ore, hot or somewhat cooled, is dumped into the storage bin, arranged for cooling, from which it may be fed to the magnetic separator as desired. If the charge contains coal or coke, the coal or coke is separated from the ash, and may be reused. If the slimes are sintered, the coarser sinter will form an excellent permeable bed to support the general charge, and the size can be so controlled that the coarse sinter sands forming the permeable bed will be metalized in about the same time as the general charge, including the fine deslimed sands at the top.

In operating the process, in the preferred way, for the production of sponge iron or metallic zinc from their oxides, for example, the three treating furnaces as shown in Fig. 2 may be assumed to be charged with the classified ore or sands in different layers, with the coarser layers at the bottom and the fine sands, with the slimes removed, on top. A coarse gas permeable material forms the lower layer of the charge. The gas permeable bed may be a layer of very coarse ore; or, if necessary or desirable, it may be a layer of coarse coke or inert refractory material, which may be used in successive charges. The slimes may be agglomerated and charged with the sands. The object is to form a charge in which the hot gas can be uniformly distributed below the mass of the ore, and then percolated uniformly through the ore. The first charge is heated by passing any cheaply heated gas, either from the heat exchanger or from the heating furnace, through the stationary charge from the bottom to the top. Until the charge is heated, the cold gas issuing from the first treating furnace, may be wasted. After the charge is heated the hot gas from the first treating furnace is passed through the charge in the second treating furnace, and so on for the third. After the first charge is heated to about the reacting temperature with the reducing gas, the preheating gas is shut off and the reducing, or reacting gas, heated to the reacting temperature in the electric furnace, passed through the reducer if necessary, is introduced into the gas permeable bed in the treating furnace and passed through the charge. After a short time the entire charge will be at the reacting temperature, and only enough heated reducing gas is then passed through the charge to meet the heat and reaction requirements. The hot reducing gas issuing from the first treating furnace is passed through the second treating furnace, and so for the third. A part may be recirculated between the electric furnace, the reducer, and the treating furnace to restore its full reducing qualities and maintain the reacting temperature in the treating furnace.

The treating furnace is so designed that practically none of the treated charge will adhere to it, and the grate, dumped with the charge, is easily caught on a coarse grating over the bin, or otherwise, and if the gas permeable bed is to be returned for a new charge, it may be similarly separated from the finished ore. If the grate is dumped with the charge it can easily be cleaned before using it in another charge.

After the charge is dumped, the grate is put in position in the hot furnace, and the gas permeable bed, either of coarse ore, coke, or inert material, is run from a bin into the treating furnace. Such an arrangement permits of a relatively small grate—much smaller than the bottom of the treating furnace—easily handled, and economically made of special high heat resisting metal alloy.

The treating furnace, as it is returned to the treating position, is charged successively with the classified sands from overhead storage bins, and when the cover is replaced, with the treating furnace in position, the cycle of treatment is repeated.

Except for dumping at the storage bin or melting furnace, the process will be free from dust or objectionable fumes, and the dumping will be largely in a neutral or reducing atmosphere, or it can be made so, and in a mass, so that there will be little or no reoxidation of the treated charge, even if it is dumped at the highest temperature attained in the treating furnace.

By manipulating the valves in the pipe lines, most of the process can be made continuous, and the number of treating furnaces can be proportioned to the time cycle of treatment.

Since the entire charge may be uniformly heated and gas uniformly passed through the hot charge, the size limit of the treating furnaces will be purely constructional, and the daily output of a well designed plant may be large. If, for example, the time of treatment, in the production of sponge iron, dumping the charge hot, is six hours, with a 100-ton treating furnace per charge, the daily capacity with four treating furnaces would be 1600 tons, which would compare quite favorably in magnitude with blast furnace and converter operations.

I claim:

1. A process comprising, treating ore to remove the slimes from the sands, charging the sands in a quiescent mass on a gas permeable support in a stationary treating furnace, maintaining the exterior of the charge containing walls of the treating furnace cooler than the charge being treated, heating a reacting gas to the temperature of reaction with the ore outside of the furnace, and then passing the hot reacting gas through the gas permeable support and through the undisturbed mass of deslimed sands.

2. A process comprising, treating ore to remove the slimes from the sands, charging the deslimed ore in a quiescent mass on a gas permeable support in a stationary treating furnace, preheating the ore by passing heated gas through the mass, separately heating a reacting gas to the temperature of reaction with the ore, and then without disturbing the mass of ore passing the hot reacting gas through the quiescent mass of the preheated ore.

3. A process comprising, treating ore to remove the slimes from the sands, classifying the sands, charging the classified sands in a quiescent mass in a stationary treating furnace so that the coarser sizes will be at the bottom and the finer sizes at the top, maintaining the exterior of the charge

containing walls of the treating furnace cooler than the charge being treated, heating a gaseous reagent to the temperature of reaction with the ore, and then without disturbing the charge passing the hot gaseous reagent upwardly through the charge from the coarser to the finer sizes.

4. A process comprising, treating ore to separate the slimes from the sands, classifying the sands, charging the classified sands in separate layers in a quiescent mass in a stationary treating furnace so that the coarser sands will be at the bottom and the finer sands at the top, preheating the quiescent charge by passing heated gaseous fluid through it, separately heating a gaseous reagent to the temperature of reaction with the ore, and then without disturbing the charge passing the hot reacting gas upwardly through the preheated charge.

5. A process of reducing ore comprising, treating the ore to remove the slimes from the sands, charging the sands in a quiescent mass on a gas permeable support in a stationary treating furnace, maintaining the exterior of the charge containing walls of the treating furnace cooler than the charge being treated, heating a reducing gas to the temperature of reaction with the ore, and then passing the hot reducing gas through the gas permeable support and through the undisturbed mass of deslimed sands.

6. An ore reducing process comprising, treating ore to remove the slimes from the sands, charging the deslimed ore in a quiescent mass on a gas permeable support in a stationary treating furnace, preheating the ore by passing heated gas through the mass, heating a reducing gas to the temperature of reaction with the ore, and then without disturbing the mass of sands passing the hot reducing gas through the quiescent mass of preheated sands.

7. A process of reducing ore comprising, treating the ore to remove the slimes from the sands, classifying the sands, charging the classified sands in a quiescent mass in a stationary treating furnace so that the coarser sizes will be at the bottom and the finer sizes at the top, maintaining the exterior of the charge containing the walls of the treating furnace cooler than the charge being treated, heating a gaseous reducing agent to the temperature of reaction with the ore, and then without disturbing the charge passing the hot reducing gas upwardly through the charge from the coarser to the finer sizes.

8. An ore reducing process comprising, treating the ore to separate the slimes from the sands, classifying the sands, charging the classified sands in separate layers in a quiescent mass in a stationary treating furnace so that the coarser sands will be at the bottom and the finer sands at the top, preheating the quiescent charge by passing heated gaseous fluid through it, separately heating a gaseous reducing agent to the temperature of reaction with the ore, and then without disturbing the charge passing the hot gaseous reducing agent upwardly through the preheated charge.

9. An ore reducing process to recover the metal therefrom comprising, treating the ore to separate the slimes from the sands, classifying the sands, charging the classified sands in separate layers in a rotatably mounted treating furnace so that the coarser sands will be at the bottom and the finer sands at the top, heating reducing gas to at least the temperature of reaction with the ore, then without disturbing the ore during treatment passing the hot reducing gas through the ore charge from the coarser to the finer sizes, and when the treatment is completed rotating the furnace and dumping the charge.

10. A metallurgical apparatus adapted to contain a quiescent mass of the material to be treated with a gas, a gas permeable support for the material in the treating furnace, a gas producer, an electric gas heating furnace comprising a resistor embedded in a gas permeable mass of inert refractory material for heating the gas from the gas producer to at least the temperature of reaction with the material to be treated, and means for causing a flow of the gas from the producer through the electric heater, through the gas permeable support and through the mass of the material in the treating furnace and means for controlling the temperature of the gas introduced into the mass of the material being treated by controlling the flow of current through the electric resistors in the gas heating furnace.

11. An ore treating apparatus comprising, a rotatably mounted treating furnace adapted to contain a quiescent and stationary charge of the ore to be treated, an electric gas heating furnace comprising a resistor embedded in a mass of inert refractory material for heating reacting gas, means for controlling the temperature of the inert refractory material and the gas by controlling the flow of electric current through the resistors, means for passing the heated gas through the quiescent and stationary mass of ore in the treating furnace, and means for rotating the treating furnace to dump the treated charge.

12. An ore treating apparatus comprising, an ore treating furnace adapted to contain a quiescent and stationary mass of the ore, an electric gas heating furnace comprising a resistor embedded in a mass of inert refractory material to heat a reacting gas, means for controlling the temperature of the inert refractory material and the temperature of the reacting gas by controlling the flow of electric current through the resistor, and means for introducing the hot reacting gas into the lower part of the treating furnace and passing it upwardly through the ore.

13. An ore treating process comprising, treating the ore to separate the slimes from the sands, charging the deslimed sands in a quiescent mass in a stationary rotatably mounted treating furnace, heating reacting gas to at least the temperature of reaction with the ore, then passing the hot reacting gas through the quiescent and stationary ore mass, and then when the treatment is completed rotating the furnace and dumping the charge.

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