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PROCESS FOR BENEFICIATION OF
MANGANESE ORES

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This invention is a novel process for the beneficiation of manganese ores, providing methods of treatment to enrich or improve the more widely existing manganese ores, especially those of relatively low grade, namely, by means of transformations or reductions, especially of the more difficultly recoverable components, preparatory to the extractions thereof; the general object being to enable profitable economic competition with the prevailing processes, the uses of which are at present almost wholly confined to the treatment of ores of relatively high grade or containing mainly the more easily recoverable components.

Ores containing manganese are known to occur plentifully and widely in many regions and countries of the world, whereas only a relatively small extent thereof has been economically exploited, the mining and extraction of manganese being confined to those special ores which are known to be rich in the metal or well adapted to be economically worked. By reason of general developments over a number of years past manganese has become one of the more highly important of the non-ferrous metals, and has entered into a great variety of applications in modern industry, one of its more important fields of utility being its employment as a component of various alloys, as in combination with iron or copper or nickel, devised for various alloy properties and practical uses. It has therefore long since become of considerable importance to be able to obtain by economical methods the manganese constituents of ores of the lower grades, heretofore falling below the class of those which have been available for profitable working by the methods or systems heretofore in prevailing use.

The general object of the present invention, therefore, is to afford a process of beneficiation of manganese ores which is well adapted to the profitable working of ores of low grade, but which naturally may if desired be employed upon richer ores. A particular object is to afford such a process adapted to economic operation for various ores, in spite of the variation in the kinds of manganese components contained in the respective ores, and in the great variation in the kinds of other materials or mineral gangues present, and in the proportions or quantities of the manganese components per ton of ore, as shown in each case by analysis.

A further object is to afford a process such as indicated which is adapted to operation by means of known types of apparatus or machinery, or indeed to be carried out by the use of existing plants laid out on prevailing principles of opera-

tion. Further objects include the providing of a mode of beneficiation or treatment in which the number of successive steps or operations is minimized, and the successive results secured by treatment at minimum temperatures; also to bring about a maximum yield of the manganese or the desired compound thereof, also to provide a process or system which can be performed continuously, in a suitably designed plant, from the input of the raw material or ore to the output of the final manganese product; and so to carry out the process as to make it practicable to recover from the raw materials other desirable products than manganese, so that the manganese may be considered as a by-product of such other products, or vice versa.

Other and further objects and advantages of the invention will be explained in the hereinafter following description of one or more embodiments of the invention or will be understood to those conversant to the subject. To the attainment of such objects and advantages the present invention consists in the herein described process for the beneficiation of manganese ore, and in various features of procedure, step, agents, reactions, intermediate and final products and by-products herein disclosed.

To bring about the general objects of the invention it is necessary to treat the poorer ores by what has become known as enrichment, or beneficiation, whereby such ore becomes converted to one of a higher grade or having a manganese value equivalent thereto. This general problem has been recognized and certain efforts have been made to solve it, but without satisfactory results in a commercial sense as distinguished from laboratory or pilot operations. One of the systems attempted for this purpose is that of fusion of the manganese ore followed by separation or reduction steps, but such system is prohibitive in expense and otherwise. Another attempt consisted in the crushing or grinding of the ore and thereupon seeking to separate out its useful part on wet concentration or on flotation principles; another effort having involved the application of magnetic separation principles directly to the ground ore. The present invention is on a different system, as will be explained, believed to be novel, and which is practically adapted to secure the desired results.

The general principles of the present invention involve special treatments, such as those to be described, by which the manganese compounds that are more difficultly extractable from the ore are, during the process, transformed into com-

pounds which are more easily extractable from the material being treated. A differentiation between compounds is thus set up, and the two classes or groups of manganese compounds may, for the purposes of the disclosed process, be designated as follows. The more readily extractable compounds, both of which have appreciable magnetic properties, include:

MnO or manganous oxide, found in the mineral manganosite.

Mn₂O₃ or manganous oxide, found in the relatively rare mineral hausmannite; this compound being known to be a combination of MnO manganous oxide and Mn₂O₃ manganic oxide and otherwise known as manganous-manganic oxide.

Among the more difficultly extractable manganese compounds are the following oxides:

MnO₂ or manganese dioxide, occurring for example in the mineral pyrolusite or in other minerals, combined for example with H₂O or with the oxides of barium, lithium, potassium or manganese.

Mn₂O₃ or manganic oxide, found in the mineral braunite, or carunite.

To this list may be added compounds other than oxides, such as the carbonate MnCO₃ found in rhodochrosite; the silicate MnSiO₃ in rhodonite, the sulfide MnS, in alabandite, and so forth.

With this background of data the process of this invention may now be first outlined as to the general character of its successive steps, adapted to be performed continuously, it being understood that such steps, and the ingredients, agents and conditions during each step are subject to suitable adaptation to each instance in hand, according to the qualitative and quantitative analysis of the ore to be treated. The preferred steps may be enumerated in sequence as follows, with further details left to more full disclosure further below:

(1) The crushing step; the order being powdered to a fine condition, for example of the order of 40 mesh.

(2) Washing in alkaline solution; the powder being put through washing operations, as with weak limewater.

(3) Mixing with carbon powder; consisting of forming an intimate mixture with powdered coke, and preferably with an auxiliary agent or alkali, as calcium hydrate or lime.

(4) Heating the mix in a non-oxidizing atmosphere; using preferably steam rather than hydrogen, at a temperature not above about 500° and preferably somewhat lower; by this step the less easily being reduced to the more easily extractable compounds, MnO₂ being reduced by the carbon to MnO etc.

(5) Quenching in neutral liquid as cold water; the hot products being passed from the heating step directly into the water bath sealed against the presence of air or oxygen, thus fixing the composition of the transformed compounds.

(6) Extracting the MnO and Mn₂O₃; preferably by dissolving in a suitable solvent such as ammonium chloride or, as an organic solvent, tartaric acid.

(7) Recovering these manganese compounds in solid form; this would usually be desirable and is readily accomplished as by evaporating or distilling off the solvent liquid, thus leaving the compounds in the form of a dry powder or amorphous product, constituting the beneficiated material resulting from the process. This final product of the present process is ready for the many modern applications of manganese; and it

compares very favorably with, and may be superior to, the highest grades of natural ores with which the enriched product must compete; besides which the process has the great advantage of ridding the product of the troublesome impurities originally present, including small amounts of copper, phosphorus, etcetera. In recovering the solid compounds from the solvent the latter may often be conserved by condensation and repeated use.

The successive steps thus outlined include the main and characteristic parts of the process hereof for enriching manganese ores to promote economic production of the metal. Having now arrived at wet or dry products containing the MnO or Mn₂O₃, or both, the process is finished; and it remains only to recover from these products, directly or indirectly, and by known or other methods unnecessary to describe, the element manganese in metallic or other desired form. The present process is adapted to afford the maximum utilization and minimum loss of manganese compounds occurring in low grade ores. The reactions involving the oxides have been above indicated; while certain of the other manganese compounds mentioned pass through similar reactions. In the case of the sulfide MnS, this requires a preliminary treatment, such as heating in the presence of oxygen, thus being converted to MnO while SO₂ passes off as a gas, the resultant being then subjected to the heating and subsequent steps of the present invention.

There is one aspect of the process not covered in the above outline, and this refers to the possible presence of iron compounds in the ore. Iron and manganese have certain properties in common and certain parallels in their compounds; so that in passing the ore through the outlined steps certain iron compounds are likely to follow reactions similar to those of the manganese compounds, with the result that by the extraction step there may be taken into the solution not only the desired manganese but certain iron compounds. This condition however is readily taken care of and the manganese and iron readily separated by supplemental steps, as will be completely set forth later in this specification. It must be observed however that it is quite permissible in many cases to turn out such a mixture or combination, since in subsequently compounding any desired iron alloys containing manganese the presence of iron with the manganese is manifestly unobjectionable, so long as relative proportions of the two are accurately known. This statement is notably true and pertinent with the present invention since the manganese-iron product is unusually pure, especially being free of even traces of such impurities as phosphorus and copper, which may seriously impair the desired alloys.

The several steps above outlined will now be disclosed and explained more fully in regard to their preferred details:

(1) The crushing step may be performed in any type of crushing or reducing mill, such as a ball mill adapted to grind the ore into a powder, preferably finer than 20 mesh, and 40 mesh being satisfactory. The apparatus should be such as to permit substantially continuous operation in the infed of broken ore, progress through the mill during crushing, and continuous delivery to the next step or stage of the process. Before or after the crushing the material may be dressed, for mechanical removal of part of the gangue, in known ways.

(2) The washing step serves not merely to cleanse the ore powder of dust and soluble matters but also to prepare its condition for the heating step by the introduction of an alkali. As an example weak limewater in cold condition may be the washing material with a strength, per ton of water, of about 1850 grams of dry calcium hydrate, or 50% more or less. This step may be performed in a conventional washing apparatus adapted for continuous operation, the crushed ore entering at one point and being delivered continuously at another point for the following stage. The lime improves the material by de-acidifying it and the water assists later in excluding air during the heating.

(3) The mixing step is to bring together the ore and the agents taking part in the hot reactions. These may be placed in a mixing apparatus or tumbling machine adapted to bring about an intimate mixing of the materials in a continuous manner, during travel from an inlet to an outlet. While the mixing may be in dry condition, preferably the ore is introduced in its previously wet condition.

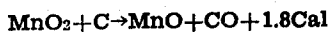
The other ingredients of the mix include compounds adapted to take part in the conversion of certain manganese compounds into others which are more easily extractable. A main ingredient for this purpose consists of a powdered carbon, preferably in the form of a coke of a kind adapted to low temperature carbonization, well adapted to reduce certain manganese compounds by removing oxygen therefrom. For example the powdered coke may be, by weight, between 5 and 15 percent of the ore, or an average of about 10 percent, dependent however upon the richness of the ore. Another suitable agent of the mix is a basic hydrate, preferably slaked lime or calcium hydrate, $\text{Ca}(\text{OH})_2$, which may constitute between 3 and 10 percent or an average of about 5 percent of the weight of the ore.

(4) The heating step may be performed in a continuous furnace such as a kiln through which travels a conveyor for progressive feed of the mix carried in the form of a shallow bed. The heating is preferably external to the chamber shell so as to avoid flames in the pressure of the mix. The purpose being to heat-treat the mixture, the temperature, while hot, is insufficient to cause fusion but is high enough to bring about chemical changes and thereby convert the manganese materials to a more suitable form or condition for subsequent extraction and separation. In part the chemical changes include reduction of certain of the oxides to others of lower oxygen content, the latter being more readily extractable from the mix, as will be further explained.

As an example the mixture, containing the manganese ore, the coke, and the calcium hydrate, may contain the higher manganese oxides, the dioxide MnO_2 and the manganic oxide Mn_2O_3 and during the treatment these will be reduced to the lower oxides, the manganous oxide Mn_3O_4 or manganous oxide MnO which are less difficultly extractable. The furnace must be such as to protect the operation from access by air or oxygen, conveniently accomplished by passing through the furnace a current of superheated steam; although a more inert atmosphere may be used, as nitrogen. The temperature of the heating treatment should be maintained between about 400° and 500° C., preferably in the neighborhood of 500° but not substantially higher than that. Calcium hydrate gives up its water

of constitution at 580° , and the temperature should be well below that, although high enough for effective heating without undue prolongation of the treatment; and it should never reach the dissociation point of steam.

The reactions under the heating temperature specified are such as to minimize or avoid the formation of manganic oxide Mn_2O_3 which is difficult of extraction. At these temperatures the manganous oxide Mn_3O_4 can not yield Mn_2O_3 , and when properly conducted this step affords as the main or only products the manganous and manganous oxides. A common constituent of the more plentiful ores is the dioxide MnO_2 , and this becomes reduced to MnO manganous oxide by the following reaction:



In connection with this reaction it should be explained that in a hydrogen atmosphere, at about 360° , the dioxide can yield manganous oxide, by the following reaction:



while the manganous oxide may become converted at red heat to the manganous oxide as follows:



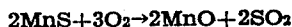
The manganic oxide Mn_2O_3 , being less easily extractable, is to be converted, which may be by the following reaction, in the present process, yielding the desirable manganous oxide:



or the manganic oxide may be converted to the manganous oxide under suitable conditions as follows:



Certain other manganese compounds in the ore, as the carbonate and silicate, may be analogously converted to MnO or Mn_3O_4 , under suitable conditions; but manganous sulfide should be previously converted, as a preparatory step, allowing plenty of time, to manganous oxide as follows:



Thus the greater portion of all manganese compounds in the ore can be brought to the composition of the manganous or manganous oxides.

Steam is a peculiarly advantageous atmosphere for the reducing operation, and its presence accelerates the reaction $\text{MnO}_2 + \text{C} \rightarrow \text{MnO} + \text{CO}$. It is believed that in the presence of H_2O , an intermediate product is formed, $\text{Mn}(\text{OH})_2$, which at once transforms to MnO , the carbon combining with the released oxygen, and the steam being restored, without undergoing dissociation. The reaction which yields MnO is aided also by the lime, whether or not the steam atmosphere be used. The lime moderates or affects the reduction and ensures that the reaction occurs in the correct direction. A particular utility resides in using in combination the steam atmosphere and the lime agent mixed with the ore and coke.

An important factor in the present process lies in keeping the ore as a powder, avoiding smelting and fusion. This is secured by working with low temperature carbonization coke, which is quite active at the preferred heating temperatures, which should not be substantially below 400° nor above 500° , and are preferably somewhat under 500° .

It should be stated that the reactions described

do not necessarily all terminate during the heating step but may extend into the cooling or quenching step. The Mn_3O_4 is believed structurally to be $MnO \cdot Mn_2O_3$, and the desirable combining of MnO and Mn_2O_3 into Mn_3O_4 takes place not at the higher temperatures but only as these components are cooled down in mutual contact.

(5) The quenching step consists of a preferably quick return of the heated and converted materials to cool temperature. Preferably the hot mixture is continuously transferred directly from the furnace to the cooling liquid or water, in a convenient vessel, the protection of the material from oxidation being continued during the transfer and cooling. By this step the reactions are completed and the desired compositions of manganese are fixed. The cooled materials may be caused to progress in any known manner continuously through the cooling apparatus, wherein the water must of course be retained in cool condition, preferably by circulation.

(6) The step of extraction of the manganous oxide and the manganosic oxide is now simply and easily performed, at low or even room temperatures; the extraction consisting in lixiviation or dissolution of these compounds out of the ore material. The bath or solvent may be provided in a vessel wherein is progressive advance, permitting continuous operation. Various solvents are readily selected; and as an inorganic solvent is preferred ammonium chloride, a suitable organic solvent being tartaric acid. In any case the solvent may be in aqueous solution, preferably quite strong, or nearly saturated.

Manganous oxide readily dissolved in the solutions of these agents, for example NH_4Cl , in strong solution in water. Manganosic oxide can be dissolved in hot concentrated phosphoric or acetic acid, or in cold concentrated sulphuric hydrochloric or oxalic acid. But it is likewise soluble at cool temperatures in the described ammonium chloride or tartaric acid solution, and without the effect of neutralizing the latter. Tartaric acid $C_4H_6O_6$ possesses the molecular weight of 150, and specific gravity of 1.76, being a solid which melts at 170° and thereupon decomposes. It is to be used preferably in solution in water or in acetic acid, tending to form the manganese tartrate $MnC_4H_4O_6$, but being recoverable for reuse. Other advantageous solvents comprise certain other organic acids which are liquid at low or room temperatures, including oleic acid, stearic acid and benzoic acid, or mixtures thereof. With any of these or other like solvents the extraction may usually be very complete, and as high as above 99 percent.

(7) There remains to be described the recovery from the lixiviating solution of the final manganese compounds. This is readily accomplished in the cases of ammonium chloride or tartaric acid by known removal or recovery methods. In the cases of oleic, stearic or benzoic acids, the recovery may be by evaporating away the solvents, at temperatures well below 400° , preferably followed by condensation, such distillation permitting recovery of each solvent for recirculation again in this step of the process. The separation in any case is preferably performed in a type of apparatus which can be coordinated with a continuous total system. On separating the liquid or solvent away from the dissolved solids the latter, usually in amorphous form, constitute the final or enriched product of the process of this invention, ready for usual or other

further treatments, as for the production of metallic manganese.

Coming now to the case where the manganese ores contain a measurable proportion of iron compounds and where it is undesirable to produce an end product which is a combination or mixture of iron and manganese, the separation thereof may be effected by known magnetic methods, for example as follows. There are several known types of magnetic separator adapted for operation upon powdered materials containing magnetic and non-magnetic components or components of differing degrees of magnetic properties. Such principles are preferably applied, for the purposes of the present invention, in advance of the extraction step, in other words between steps (5) and (6), as enumerated above; although the separation could be performed instead after obtaining the final extracted and dried solid product.

As already mentioned the small percentages of iron compound in the ore are likely to pass through conversions similar to those of the manganese, with the result that, following the heating and quenching steps (4) and (5) the iron will exist in the form of ferrous oxide FeO or ferrosic (ferrous-ferric) oxide Fe_3O_4 , corresponding in formula with the more easily extractable oxides of manganese. Fe_3O_4 , obtained from the mineral magnetite has perhaps the best magnetic susceptibility of the iron compounds, while both of the iron oxides mentioned have far greater susceptibility, or magnetizability, than the corresponding manganese oxides, which points the way to the separation thereof. In carrying out this step the powdered material, preferably passing continuously through the magnetic separator, is subjected first to a carefully adjusted magnetic action of relatively low intensity, the degree of which is determined to draw away from the mixture all particles of the iron compounds present, while being somewhat too weak to cause any effective displacement of the manganese compounds. In this way the iron compounds are diverted for separate discharge from the apparatus, while the manganese compounds continue the advance, along with gangue and other non-magnetic material. Thereafter, at a suitable point in the progress, a stronger magnetic attraction may be applied thereby to divert the manganese compounds for discharge independently of the other components of the mixture; although this is unnecessary if the entire powdered mixture, minus the iron component, is lixiviated for extraction of the manganese component into solution, as already described.

Certain considerations in respect to the described process may be supplementally referred to as follows: The step (3) of mixing the three materials while described as following after the crushing step (1) and the washing step (2), may obviously precede the washing, or even precede the crushing, so long as the complete mixture in a finely divided condition enters the chamber or kiln for the heating step. The purpose and action of the active carbon in the mixture is to constitute a solid reducing agent, converting the higher to the lower oxides of manganese. In operation the basic hydrate or lime $Ca(OH)_2$ functions not only to promote such conversion of oxides, but to effect the conversion of manganese silicate $MnSiO_3$ which, at the elevated temperature and in the presence of the hydrated lime, reacts to form MnO and calcium silicate and water. Manganese carbonate $MnCO_3$ disin-

tegrates at the working temperature into MnO and CO₂. For the quenching step (5) not merely water but any inactive liquid may naturally be made use of. The extracting step (6) for separating the reduced compounds from the finely divided mixture, was above first stated to be preferably by dissolving the reduced manganese compounds in a solvent; but magnetic separation was mentioned as another mode, used in a way first to remove the iron compounds, and then the manganese compounds, from the mixture or gangue; and naturally other separating modes may be used, such as classification by gravity with floating up and away of the lighter minerals from the heavier metal compounds.

A process for the beneficiation of manganese ores has thus been described which embodies the principles and attains the objects of the present invention, but since many matters of operation, steps and order thereof, specific reactions, and character of compositions used may be variously modified without departing from the principles of the invention, it is not intended to limit the patent to such matters except to the extent set forth in the respective appended claims.

What is claimed is:

1. A process for beneficiating or enriching a manganese ore comprising first crushing the ore to a powder; washing the powdered ore in an alkaline solution as of weak lime water; mixing intimately the washed powder with powdered active carbon or coke, such as low temperature carbonization coke, in substantial proportion between about five and fifteen per cent by weight, and with an auxiliary alkaline agent consisting of a basic hydrate in a somewhat lower proportion; treating the mixture at a temperature between about 400° and 500° in a non-oxidizing atmosphere as steam, for a period sufficient to transform or reduce the manganic oxide and manganese dioxide present to the form of manganous oxide or manganosic oxide; quenching or cooling the roasted mixture to fix the transformed compositions; extracting from the mixture the manganous oxide and manganosic oxide by a liquid solvent; and recovering such extracted compounds in the solid form of enriched manganese material adapted to further treatment.

2. A continuous process for enriching a manganese ore after crushing to a powder, comprising mixing intimately the ore powder with powdered active carbon, and with a basic hydrate, in substantial proportion, heating the mixture at a reaction temperature substantially not above about 500° in a non-oxidizing atmosphere, until the manganic oxide and/or manganese dioxide present are reduced to manganous oxide and/or manganosic oxide; cooling the hot mixture while preventing oxidation thereby to fix the reduced compounds; extracting from the mixture by liquid solvent the manganous oxide and/or manganosic oxide; and recovering from the liquid such extracted compounds in the form of enriched manganese solids adapted to further treatment.

3. A process for enriching a crushed manganese ore, comprising mixing intimately the ore powder with powdered reactive carbon and with calcium hydrate, each in substantial proportion, heating the mixture at a reaction temperature substantially not below 400° nor above about 500° in a non-oxidizing atmosphere including steam, until any manganic oxide and manganese dioxide present are reduced to manganous oxide and/or manganosic oxide; cooling the roasted mixture while

preventing oxidation thereby to fix the reduced compounds; and extracting from the mixture and recovering the manganous oxide and manganosic oxide.

4. A process for enriching a manganese ore supplied as a powder, comprising mixing intimately with the ore powder substantial proportions of powdered low temperature carbonization coke and slaked lime, heating the mixture at a hot reaction temperature not substantially above about 500° in a non-oxidizing atmosphere, as steam, until the more difficultly extractable manganese compounds present are reduced to the more easily extractable oxides; then cooling the hot mixture while preventing oxidation, thereby to fix the reduced compounds; and extracting from the mixture by lixiviation the reduced oxides.

5. The process as in claim 4 and wherein MnO₂ by the carbon becomes reduced to MnO plus CO.

6. The process as in claim 4 and wherein Mn₂O₃ by combination with MnO is reduced to Mn₃O₄.

7. The process as in claim 4 and wherein the lixiviation is carried out by tartaric acid, capable of dissolving MnO and Mn₂O₃.

8. A process for enriching a manganese ore in powder form, comprising mixing intimately with the ore powder a substantial proportion of powdered coke, and a lesser proportion of a basic hydrate, as slaked lime, heating the mixture at a hot reducing temperature not substantially above about 500° in an atmosphere of superheated steam, then cooling the mixture while preventing oxidation, thereby to fix the reduced compounds; and extracting from the mixture such reduced compounds.

9. A process for enriching a ground manganese ore comprising mixing intimately with the ore powder a proportion of carbon in about 5 to 15 percent of the ore and a basic hydrate in about 3 to 10 percent of the ore, heating the mixture at a hot reaction temperature not substantially above about 500° in a non-oxidizing atmosphere, as steam, until the more difficultly extractable manganese compounds present are reduced to the more easily reducible oxides; then quenching the hot mixture while preventing oxidation, thereby to fix the reduced compounds; and extracting and recovering the reduced oxides.

10. The process as in claim 4 and wherein the manganous and manganosic oxides are extracted from the heat-treated ore mixture by means of a liquid solvent that is capable of distillation, whereby the solvent may be evaporated for the recovery of the solids and the solvent condensed for its recovery and re-use.

11. The process as in claim 4 and wherein the manganous and manganosic oxides are extracted from the heat-treated ore mixture by means of a liquid solvent that is capable of distillation, selected from the group consisting of oleic acid, stearic acid and benzoic acid and mixtures containing one or more thereof.

12. The process as in claim 8 and wherein the ore contains manganese silicate, which during heat treatment is converted by reaction with the slaked lime to manganous oxide.

13. The process for beneficiation of manganese ore comprising the steps of mixing the ore with minor proportions of a solid reducing agent as carbon and of a basic hydrate as slaked lime, and treating such mixture in finely divided condition by subjecting it to heating in a non-oxidizing atmosphere in a closed chamber or kiln at a reaction temperature not above about 500° C.,

thereby to maintain its finely divided condition, and for a substantial duration until terminated by quenching rapidly the mixture in liquid while continuing the prevention of oxidation; whereby during such heating and quenching treatment substantially all of the more difficultly extractable manganese compounds present, including manganese dioxide MnO_2 and manganic oxide Mn_2O_3 , are converted or reduced to the more easily extractable manganous oxide MnO and manganosic oxide Mn_3O_4 , and such quenching serving to fix such conversion compounds; and thereafter suitably separating from the finely divided mixture and recovering such conversion compounds in solid form.

14. The process as in claim 12 and wherein the basic hydrate is slaked lime, which can retain its water of constitution at the heating temperature, and which promotes the desired conversion reaction and reacts also with any manganese silicate $MnSiO_3$ to convert the manganese thereof to an oxide.

15. The process as in claim 12 and wherein the carbon is in proportion by weight of about 5 to 15 percent of the ore, while the basic hy-

drate is in proportion of about 3 to 10 percent of the ore.

16. The process as in claim 12 and wherein the treating temperature is maintained somewhat below 500° but not below 400° .

17. The process as in claim 12 and wherein for the non-oxidizing atmosphere is used steam, adapted to resist dissociation at the temperature stated.

18. The process as in claim 12 and wherein the ore may contain manganese carbonate $MnCO_3$, which becomes converted in the process to the more easily extractable compounds mentioned.

19. The process as in claim 12 and wherein the ore may contain manganese sulfide MnS , in which case such sulfide is first by preliminary step converted to manganous oxide MnO .

20. The process as in claim 12 and wherein the ore may contain iron oxides, in which case the iron may be separated out of the mixture after the quenching step but before the extraction step, by weak magnetic action, as in known types of magnetic separator.

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CERTIFICATE OF CORRECTION.

Patent No. 2,296,841.

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It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 6, first column, lines 16 and 23, and second column, lines 3, 6, 10, 14 and 18, claims 14 to 20 inclusive, for "claim 12" read --claim 13--; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 3rd day of November, A. D. 1942.

Henry Van Arsdale,
Acting Commissioner of Patents.