

June 9, 1959

C. C. DAUGHERTY

2,890,104

RECOVERY OF MANGANESE FROM ORES

Filed Nov. 13, 1957

2 Sheets-Sheet 1

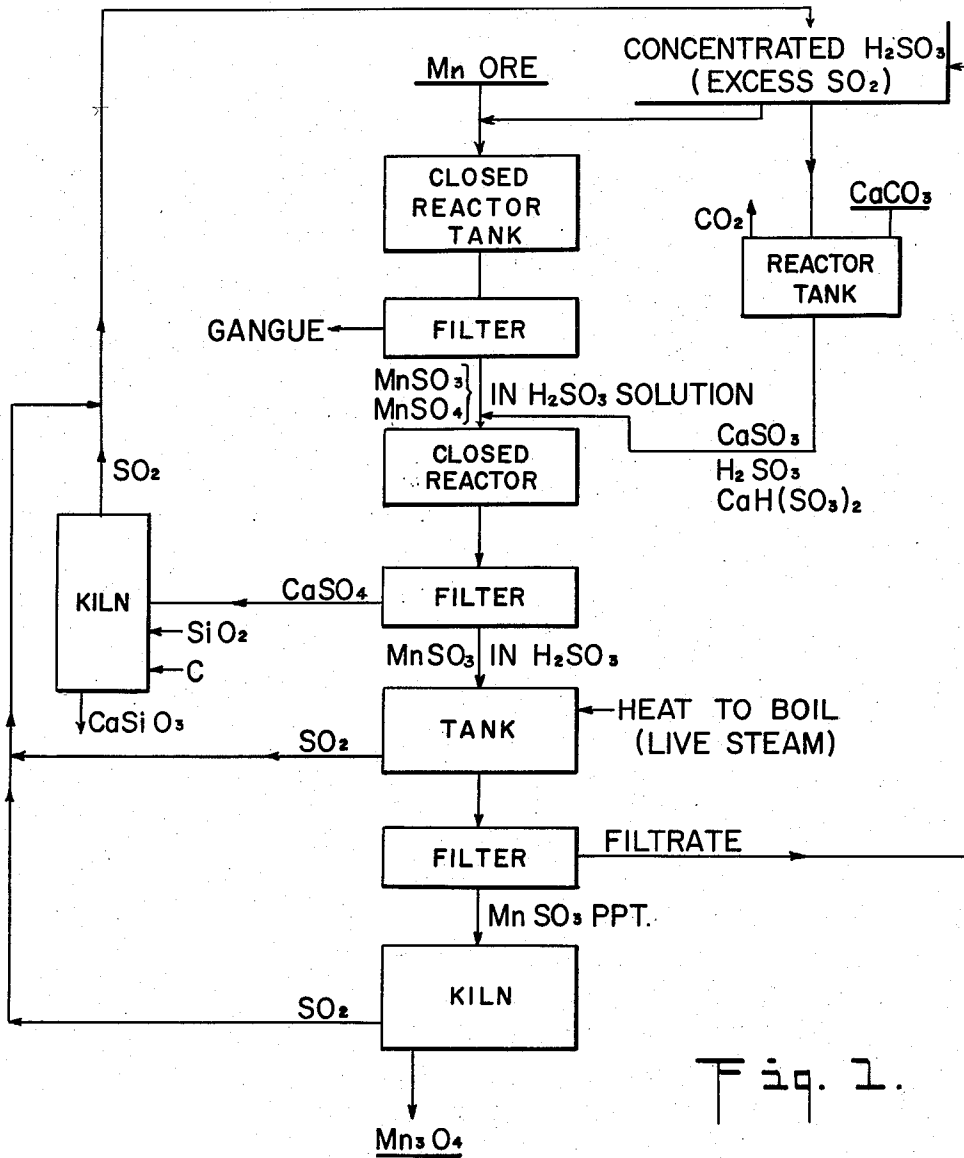


Fig. 1.

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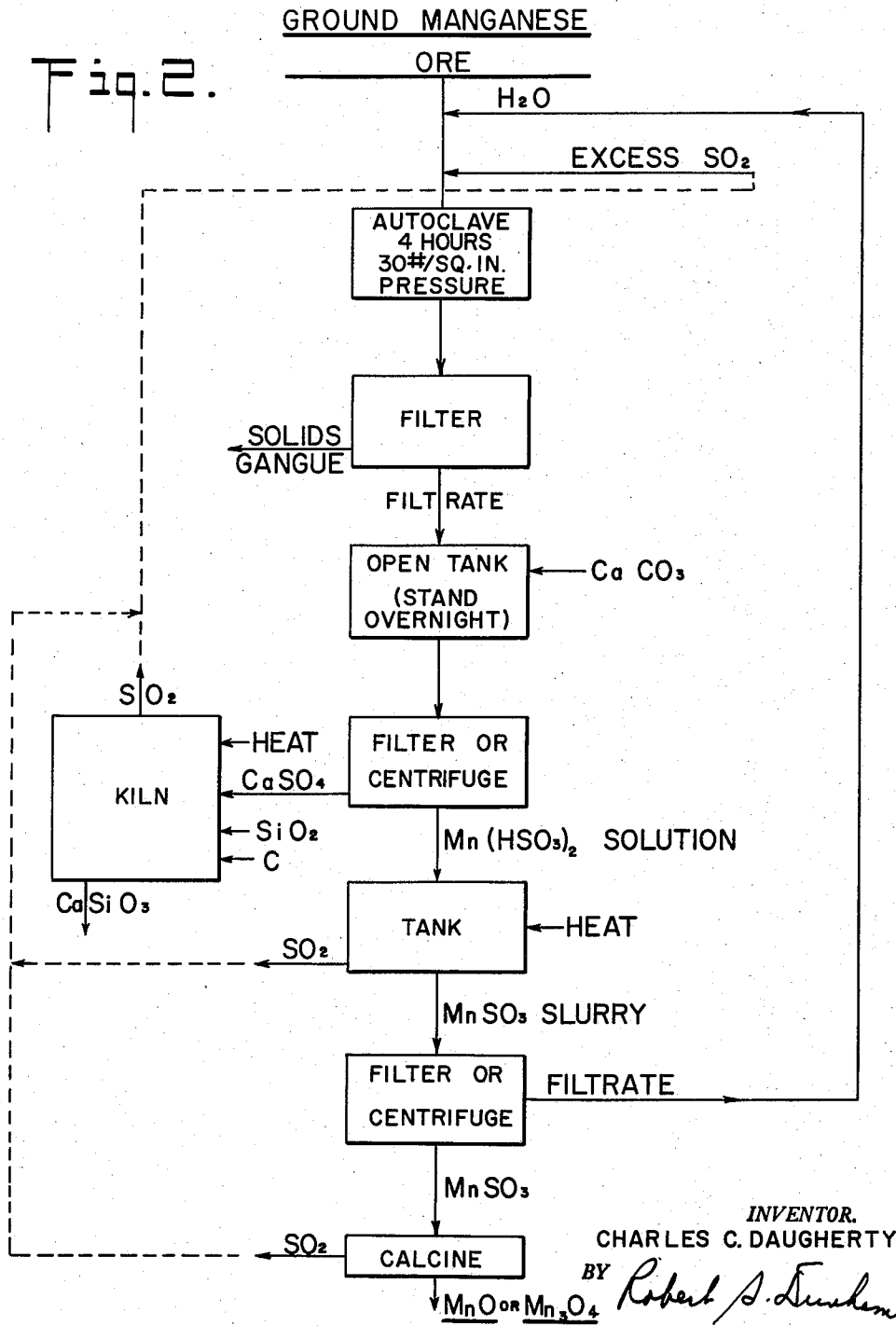
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2 Sheets-Sheet 2



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2,890,104

RECOVERY OF MANGANESE FROM ORES

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Application November 13, 1957, Serial No. 696,285

7 Claims. (Cl. 23—145)

This invention relates to a method of extracting and recovering manganese values from ores, and specifically from low grade ores, which may not contain more than about 15% or 20% manganese and which often assay as little as 10% to 12% manganese or less. More particularly, the invention is directed to procedures for separating and concentrating manganese from ores which are of the character described above, which contain manganese in different valence states, and which also contain other metallic values, specifically iron, usually in an amount greater than the amount of manganese present.

As such, the present invention is a continuation-in-part of my prior and copending application Serial No. 406,545, filed January 27, 1954 and having the same title, this application being now abandoned. The present invention is also related to and constitutes an improvement upon my invention relating to a process of recovery of manganese from ores described and claimed in Patent No. 2,747,965 issued May 29, 1956.

The present application is also related to an application being filed concurrently herewith and identified as Serial No. 696,284, filed November 13, 1957, which is a continuation-in-part of my application Serial No. 406,521, filed January 27, 1954 and now abandoned, but which was copending with my application Serial No. 406,545 aforesaid. The line of division between the present application and said application Serial No. 696,284 is based upon the principle that said application Serial No. 696,284 contains all claim subject matter common to these two cases; while the present application contains only claims readable upon this present application and not supported by the disclosure of said application Serial No. 696,284.

Although the methods described herein are applicable to ores of the stated character from other regions, they have been developed and are found particularly successful for the treatment of manganiferous minerals found in Maine, especially in the deposits of Aroostock County. These Maine ores have a high phosphorus as well as a large iron content, and because of the phosphorus, pyrometallurgical treatments appear unduly expensive. At the same time, the chemical combination of manganese in Maine ores, apparently to a large extent as manganous carbonate and partially as silicate, or perhaps in the form of double or complex combinations of iron and manganese, is such that no effective results will be obtained with physical concentration or beneficiation methods. Indeed, some belief, which I have found erroneous, that the manganese in these ores was present in a silicate form highly refractory to any type of concentration treatment, has apparently heretofore discouraged attempts to utilize these ores as a source of manganese. In general, it may be said that these ores contain manganese in different valence states including bivalent, trivalent, and tetravalent. In the tetravalent state, it is believed that manganese is present as manganese dioxide.

A number of lots of Maine ores of the type specifically mentioned above were found to contain about 12%

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manganese, about 21% iron, and slightly less than 1% phosphorus. These ores, of this composition, were used in the examples hereinafter described in working out various phases of the present invention. Because of the relatively small amount of manganese in these ores, the cost of the recovery treatment or the economics of the present method or process is particularly important and is a primary consideration, inasmuch as the industry will pay only about a certain amount for manganese, considering the degree of purity thereof, so that the present invention must meet the commercial requirements in this respect. In other words, while it might be theoretically possible, at an unlimited expense, to recover a much larger percent of the manganese initially present and/or to recover the manganese in a very high state of chemical purity, what must be done practically is to provide a method of recovery of as much manganese as is practicable and at a state of purity (principally freedom from iron) which is similarly practicable in order that the product may be sold competitively. The provision of such a method or process is a primary object of the present invention.

There is disclosed and claimed in my patent No. 2,747,965 aforesaid a process for the recovery of manganese from ores, in which the ore is leached by a calcium chloride solution saturated with sulfur dioxide. This does not in any way come under or follow the present invention in that it is essential in order to attain the objects of the present invention that there be no soluble chloride or other compound present which will provide halide ions in solution in order that the results desired in accordance with the present invention be attained, all as hereinafter particularly set out.

In my copending application Serial No. 406,521, of which the application Serial No. 696,284, filed concurrently herewith is a continuation-in-part and substitute, a method is disclosed and claimed which to some extent is dominant over the present application. This process or method is based upon a selective treatment of the ore by leaching it with an aqueous solution, the essential active ingredients of which consist of water and sulfur dioxide, and in which oxygen and other oxidizing agents are in effect absent. In accordance with this process, at least during the leaching stage thereof, chloride is normally absent. Notwithstanding this, there is a substantial degree of selectivity which is found to exist as between the leaching of manganese and iron, so that notwithstanding an initial iron content in the ore greater than that of manganese, the leach solution is very substantially higher in manganese than in iron. To the extent of using this leaching process and taking advantage of the selectivity thereof, the present case may follow exactly the teaching of this copending application Serial No. 696,284. The novel and peculiar features of the present application as distinguished from that of Serial No. 696,284 apply particularly to the next step of the process. The only particular requirement of the present process as to the selective leaching step aforesaid (if used) is that it be accomplished by and to form a solution in which chloride and other halide ions are effectively absent, as such ions would tend to defeat the intended objects of the present invention. Thus, the present application may start with a solution including manganese in the form of sulfite and sulfate, irrespective of how that solution is formed and including, for example, the forming of the solution by a leaching operation in accordance with the teachings of my copending application Serial No. 696,284, with the proviso, however, that this solution must be substantially free of halide ions.

The starting material, therefore, for the present process is a solution containing manganese sulfite and manganese

sulfate, which solutes are maintained in solution by having the solution substantially saturated with sulfur dioxide. Under these circumstances, manganese sulfite is quite soluble. The same may be said for iron (ferrous) sulfite, which is similarly soluble in a concentrated aqueous solution of sulfur dioxide. Manganese sulfate is soluble in water as are both ferrous and ferric sulfates, whether or not that water contains dissolved sulfur dioxide. Both manganese sulfite and ferrous sulfite are relatively insoluble, or very slightly soluble, in water, so that once the excess sulfur dioxide is driven off, for example by heating, these materials will be thrown out of solution as precipitates. The solubilities of these two materials as aforesaid are known properties of these materials and no invention is predicated thereon per se at this time.

A particular feature of the present invention is to provide a method of recovering the manganese in a simple and effective manner, using relatively cheap and available ingredient and reaction materials and in a manner enabling the substantially complete recovery of sulfur dioxide, or sulfur in whatever form it may exist from time to time in the process. All this is necessary to the economic practicability of the present process.

In accordance with the present invention, it is desired that any manganese sulfate present will be converted to manganese sulfite prior to throwing this material out of solution in the saturated sulfur dioxide solution. It is known that manganese sulfite is relatively easily oxidized to manganese sulfate by the presence of oxidizing agents, including air, so that the present reaction should be done in the substantial absence of air or oxygen. Furthermore, inasmuch as the key feature of the present process is to enable manganese sulfite to be thrown out of solution as such, the process must be carried on in the substantial absence of ions which would render the manganese soluble, particular halide ions, such as chloride. For this reason, therefore, it is impossible, in accordance with this invention to resort to the expedient taught in my copending application Serial No. 696,284, filed concurrently herewith, of using calcium chloride as a reagent to react with the manganese present. On the other hand, it is found in accordance with the present invention that by treating manganese sulfate with calcium bisulfite, which is also quite soluble in water, the manganese sulfate present may be converted to manganese sulfite, with the calcium going to the very insoluble calcium sulfate. This calcium bisulfite may be generated either substantially simultaneously with the reaction thereof with the manganese sulfate or separately, the latter course being preferred. In this latter process, briefly, calcium carbonate (limestone), preferably in fine particle form, is supplied to a saturated sulfur dioxide solution, whereupon the reaction forms a slurry of calcium sulfite and a solution of calcium bisulfite. The calcium sulfite is very sparingly soluble; but once dissolved, it is believed to react to form the soluble calcium bisulfite as hereinafter set forth. This solution is then mixed with the solution containing the manganese sulfite and sulfate and an adequate time provided for the substantial completion of the reaction, resulting in the conversion of substantially all the manganese sulfate to manganese sulfite.

Alternatively, and as generally indicated above, the solution of the calcium carbonate in the saturated sulfur dioxide solution may be effected substantially simultaneously with the reaction between calcium bisulfite and manganese sulfate, the mechanism of the reactions being substantially the same and the product, identical as far as is known.

Once the reaction aforesaid, irrespective of which of the two alternatives is used, has been substantially completed, any solid materials present may be separated by conventional solid versus liquid separation techniques, including filtration, and the resulting solution, which is

now substantially solely manganese sulfite in a saturated aqueous solution of sulfur dioxide, may then be heated to drive off the excess sulfur dioxide, resulting in a precipitate of manganese sulfite. This precipitate may then be separated from the remaining solution and then calcined to give an oxide of manganese and to drive off sulfur dioxide. The sulfur dioxide driven off, both by the heating operation which precipitated the manganese sulfite and by the calcining operation in which the manganese sulfite was converted to a manganese oxide, may then be returned for reuse, for example, in the leaching step of the process. Similarly, the calcium sulfate resulting from the reaction between calcium bisulfite and manganese sulfate may be treated for the recovery of sulfur dioxide by a conventional known process, and the sulfur dioxide product thereof returned for reuse as aforesaid.

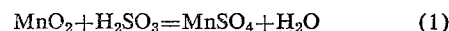
Inasmuch as the present purpose is to provide a solution of manganese sulfite in a saturated sulfur dioxide solution, so that the manganese sulfite may be thrown out of solution by boiling it for the recovery of manganese in this way, it is quite essential that any material, which will cause manganese to remain in solution after the heating step has been effected, should be absent. For this reason, therefore, it is considered essential from the point of view of the present process that there be no chloride or other halide ions in solution, as manganese chloride or other halides are quite soluble, so that to the extent that such halide ions are present, manganese would not be thrown out of solution by the heating or boiling step. The solution remaining following this heating or boiling step and the separation of the precipitated manganese sulfite therefrom is preferably returned to the leaching step of the process, so that any manganese not precipitated at this time is merely recycled in the process. Nevertheless, the presence of halide ions would continuously hinder the desired course of the process and hence should not be present, except perhaps in trace or unavoidably small amounts.

The present process or method is illustrated on a diagrammatic or flow sheet basis in the accompanying drawings, in which:

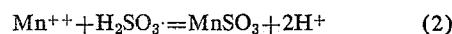
Fig. 1 is a flow sheet illustrating the presently preferred process or method according to the invention;

Fig. 2 is a flow sheet illustrating a modified process or method also embodying the invention.

The precise chemical reactions involved in the leaching step are not certainly known, particularly because of the number of compounds present during the leaching step which may form part in these reactions or which may affect them. For that reason, the invention cannot be limited to any precise theory of chemical sequence at this stage of the process or method. It is believed, however, that tetravalent manganese, probably in the form of MnO_2 , is converted to manganese sulfate by a reaction substantially as follows:



On the other hand, divalent manganese, i.e. manganese occurring in the ore in the divalent state, is believed to be converted to manganese sulfite by a reaction which is probably as follows:



Trivalent manganese is believed to be converted in part to manganese sulfite and in part to manganese sulfate by some combination of the reactions set forth in Equations 1 and 2.

It is also contemplated as a possible alternative that the original ore may be subjected to some kind of reducing action prior to the leaching step, so as to increase the amount of lower valence manganese present and correspondingly decrease the amount of higher valence forms thereof. This is set out more in detail in my copending application Serial No. 696,284 aforesaid.

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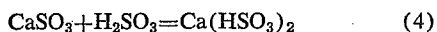
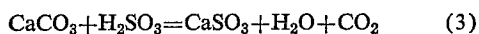
Further, during the leaching step it is found that the selectivity in leaching manganese as distinguished from iron requires that there be no oxygen or other oxidizing materials present. Again, this subject matter is described and claimed in my copending application Serial No. 696,284.

Following the leaching operation, any remaining solid materials are separated from the leaching solution. Such solid materials will include, for example, any gangue originally present with the ore, any iron compounds which are not solubilized due to the selective action of the leaching step of the method or process and any undissolved manganese. In this respect, it is found that while the leaching step will dissolve most of the manganese present, it will not dissolve it all, so that some manganese will remain undissolved and is removed as hereinafter set forth with the gangue. This is not particularly desired, but is a practical result of operating on an economical basis as to time and reagents. It is economically more advantageous, for example, to recover a large part, but not all the manganese, than it would be to try to recover it all.

It is further contemplated, as specifically taught in my copending application Serial No. 696,284, that the leaching operation may be carried on not only at atmospheric pressure and at room temperature, but also at superatmospheric pressures, at temperatures substantially above room temperature, or both. It is found that the use of higher temperatures and/or pressures result in somewhat increased yield. Thus there is present an economic balance between the additional costs of the higher temperatures and/or pressure on the one hand, as against the increased recovery of manganese on the other.

In any event, following the leaching operation, there is a separation step carried on between the remaining solid materials as aforesaid on the one hand, and the leach solution. These solid materials may be discarded in so far as the present invention is concerned. The present invention per se starts with the treatment of the leach solution following the separation thereof from the solid material.

In accordance with the preferred embodiment of the present invention, which is illustrated diagrammatically in Fig. 1 of the drawings, a reactant slurry is prepared in a separate tank or container by mixing relatively finely divided calcium carbonate with a solution of sulfurous acid, preferably a saturated solution, which may be maintained saturated by maintaining above and in contact with this solution an atmosphere consisting essentially of sulfur dioxide. While it is not essential during the preparation of this solution that oxygen be precluded from contact therewith, it is highly desirable that the oxygen content of the solution be as low as possible, as any oxygen in contact with the manganese-containing solution tends, to the extent that it is present, to defeat the desired object of the present invention. It is also highly important that this (calcium-containing) solution be maintained free or substantially free from dissolved halides or halide ions. For this reason, therefore, the solution is preferably made up under an atmosphere of sulfur dioxide by mixing calcium carbonate in finely divided and hence reactive form with the sulfur dioxide solution. It is believed that the reactions incident to the making up of this solution are substantially as follows:



In accordance with these equations, some calcium sulfite (CaSO_3) is formed. However, this material is very sparingly soluble in water, but dissolves somewhat in a sulfur dioxide solution in accordance with Equation 4. There results, therefore, a slurry including possibly some unreacted calcium carbonate, some undissolved calcium

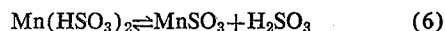
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sulfite and a solution of calcium bisulfite. The calcium bisulfite is the essential reactive material needed for the next step of the process as hereinafter set out.

The solution of calcium bisulfite admixed with solid material and in the form of a slurry and in an amount sufficient to react with all the manganese sulfate present may then be mixed with the manganese-containing solution, which is the real starting point of the present process, i.e. the saturated sulfur dioxide solution containing some manganese sulfite and some manganese sulfate. These mixed solutions are then maintained together, possibly with agitation, but in any event for a time sufficient for the substantial completion of the desired reactions. These reactions are believed to be as follows:



and there is always a balance or reversible reaction as follows:



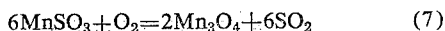
Thus, the product may be considered manganese sulfite, which is always in equilibrium in the saturated sulfur dioxide solution, with manganese bisulfite in accordance with Equation 6. It may be considered, however, that the product under all circumstances can be properly described as a solution of manganese sulfite in a saturated solution of sulfur dioxide in water. This reaction (Equation 5 above) is relatively slow; and for substantial completion, the reaction mixture should be allowed to stand for a period of perhaps twelve to fourteen hours, typically overnight. It is preferred that it be carried on in the way just described and in accordance with Fig. 1, as this manner of operation enables the process or method to be more accurately controlled than is possible in accordance with the alternative embodiment of the method illustrated in Fig. 2 and hereinafter described.

Turning now to the Fig. 2 embodiment of the process, instead of making a separate solution using calcium carbonate and a saturated solution of sulfur dioxide, it has been found feasible and is fully operative that the calcium carbonate, preferably in finely divided form, may be admixed with the solution of manganese sulfite and manganese sulfate in a saturated solution of sulfur dioxide; in other words, with the leach solution prepared as aforesaid as a typical example of the process. It is believed that the reactions occurring under these circumstances are exactly the same as those hereinabove set out for the Fig. 1 form of the invention, except, however, that all the reactions take place in the one bath or slurry and proceed to substantially the same degree of completion as if the solutions were separately prepared and then later mixed as in the Fig. 1 form of the process. Thus, it is the present belief that in either case, the reaction which is essential to the present process is one between manganese sulfate and calcium bisulfite (Equation 5 above).

At the conclusion of this reaction, i.e. after a sufficient time has been provided for the substantial conclusion thereof, the remaining solid materials, consisting of calcium compounds including any unreacted calcium carbonate, undissolved calcium sulfite and the calcium sulfate product of the reaction, are separated from the remaining solution. This may be done again by any conventional separation method such as filtration, centrifuging or other equivalent separation operation.

Following the separation step, the remaining solution, which should contain substantially solely manganese sulfite in a concentrated solution of sulfur dioxide, is subjected to heat, for example, by boiling this solution. This drives off the excess sulfur dioxide and causes the manganese sulfite to be very largely precipitated out, due to the relatively low solubility of this material in water. The sulfur dioxide evolved during this heating or boiling step may then be returned for reuse as aforesaid. The precipitated manganese sulfite may then be sep-

arated from the remaining solution by any suitable separation technique, e.g. filtration, and calcined to an oxide of manganese such as Mn_3O_4 . The calcining reaction which takes place in the presence of oxygen (air) is believed to be carried on in accordance with the following equation:



The sulfur dioxide evolved in this calcining action is also preferably returned to the process for reuse as aforesaid.

The only other place where sulfur may be lost is in the precipitated calcium sulfate resulting from the reaction between the calcium bisulfite and the manganese sulfate. This calcium sulfate may also be treated by a known process to recover sulfur dioxide, the process involving heat treatment with silica in an appropriate form and with carbon, resulting in the production of calcium silicate and sulfur dioxide. The reaction in accordance with this process is believed to be as follows:



The calcium silicate produced may, for example, be used as a raw material for the production of cement.

The process is further exemplified by the following example, in which a Maine ore having the composition aforesaid was used.

Example 1

100 grams of this ore containing 12.11 grams of manganese was leached with 500 ml. of a freshly prepared aqueous solution of sulfur dioxide containing 31.72 grams of sulfur dioxide. The leaching process was continued for three hours at room temperature and atmospheric pressure. The resulting slurry was then filtered and the filtrate assayed, showing an apparent recovery at this point of 10.4 grams of Mn or 86.0%.

19 grams of pure calcium carbonate was made into a slurry with water. SO_2 was then passed into this slurry until all of the calcium carbonate had been converted into calcium bisulfite and calcium sulfite, and enough additional SO_2 was supplied to insure saturation.

This slurry was added to the filtrate containing the manganese values and the mixture allowed to reach equilibrium, while being carefully agitated, oxidation from the air being prevented as much as possible.

After several hours the precipitate of calcium sulfate was filtered off and the filtrate stripped of its sulfur dioxide content by means of heat and vacuum. Manganese sulfite crystallized from the solution as the SO_2 was removed. This was filtered off, dried, and calcined to produce a concentrate of Mn_3O_4 and gaseous SO_2 . The concentrate contained 7.8 grams of Mn or roughly 75% of the Mn in the leach liquor. The filtrate from the last filtering step contains a substantial proportion of manganese values, and may be recycled to the leaching step to prevent loss of such values.

Thus, in accordance with the present invention, all the manganese to be recovered is either in or is brought into the form of manganese sulfite, which may be precipitated from the concentrated solution of sulfur dioxide in water by heating such solution to drive off the excess sulfur dioxide. Any manganese sulfite not precipitated at this point, due to the small but existing solubility thereof, is preferably recovered in a continuous or commercial operation by recycling the remaining solution (irrespective of the mode of separation) from this precipitation step to the leaching step of the process. This makes a much simpler recovery than is possible when operating in accordance with the teachings of either my prior patent or the copending application Serial No. 696,284 in that the manganese is all recovered at one point rather than two and in that it is unnecessary to precipitate out manganese in oxide or hydroxide form by the use of a slurry of lime.

While there is herein shown and described but one principal process and certain modified forms thereof,

other equivalents have been suggested as the description proceeded and still others will suggest themselves to those skilled in the art from the foregoing disclosure. I do not wish to be limited, therefore, except by the scope of the appended claims, which are to be construed validly as broadly as the state of the art permits.

What is claimed is:

1. The method of recovering manganese values from ores, in which manganese occurs in different valence states from 2 to 4 inclusive, comprising the steps of leaching the ore with a liquid consisting essentially of water saturated with sulfur dioxide and which is substantially free of compounds providing halide ions, said leaching also being effected in the substantial absence of oxygen, so as to convert a major portion of the manganese values of the ore to soluble form in the water-sulfur dioxide solution as manganese sulfite and manganese sulfate; separating the solution so formed from any remaining solid material; reacting the separated solution with calcium bisulfite, in the continued absence of oxygen and of dissolved compounds providing halide ions in solution and for a time sufficient to convert substantially all the manganese sulfate initially present to manganese sulfite, and so as to retain in solution in the saturated sulfur dioxide solution all the manganese sulfite present initially and that which is formed, the reaction resulting in the precipitation of calcium sulfate; separating all the undissolved material present from the remaining solution; heating said remaining solution so separated to drive off excess sulfur dioxide and thereby precipitating most of the manganese sulfite; and separating the precipitated manganese sulfite and treating it to recover manganese values therefrom.

2. The method in accordance with claim 1, in which the step of reacting the separated solution with calcium bisulfite is effected by separately preparing a slurry including dissolved calcium bisulfite by dissolving calcium carbonate in a saturated aqueous solution of sulfur dioxide, and adding the slurry so prepared to the separated solution aforesaid including manganese sulfite and manganese sulfate.

3. The method in accordance with claim 1, in which the step of reacting the separated solution with calcium bisulfite is effected by adding calcium carbonate to said separated solution, while maintaining it substantially saturated with sulfur dioxide.

4. The method of recovering manganese values from an aqueous solution which is saturated with sulfur dioxide, which is substantially free of solutes providing halide ions, and which also contain dissolved manganese in the forms of manganese sulfite and manganese sulfate; said method comprising the steps of reacting the manganese sulfate in said solution with calcium bisulfite, in the absence of oxygen and in the continued absence of solutes providing halide ions and for a time sufficient to convert substantially all the manganese sulfate initially present to manganese sulfite, while maintaining said solution saturated with sulfur dioxide, so as to maintain all the manganese sulfate initially present and that formed by the reaction in solution therein, and the reaction also resulting in the precipitation of calcium sulfate; separating all the undissolved material present from the remaining solution; heating said remaining solution so separated to drive off excess sulfur dioxide and thereby precipitating most of the manganese sulfite; and separating the precipitated manganese sulfite and treating it to recover manganese values therefrom.

5. The method in accordance with claim 4, in which the step of reacting the manganese sulfate in said solution with calcium bisulfite is effected by separately preparing a slurry including dissolved calcium bisulfite by dissolving calcium carbonate in a saturated aqueous solution of sulfur dioxide, and adding the slurry so prepared to the solution including said manganese sulfate.

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6. The method in accordance with claim 4, in which the step of reacting the manganese sulfate in said solution with calcium bisulfite is effected by adding calcium carbonate to said solution, while maintaining it substantially saturated with sulfur dioxide.

7. The method of recovering manganese values from ores containing both divalent and tetravalent manganese values, comprising the steps of leaching the ore with water saturated with sulfur dioxide and in the absence of oxygen, thereby dissolving the divalent manganese values as sulfites and the tetravalent values as sulfates, filtering the mixture to remove the gangue, mixing the resulting solution with a slurry of calcium sulfite in a solution of sulfurous acid and calcium bisulfite and in the absence of oxygen to convert the dissolved manganese sulfates to sulfites and the calcium compounds to calcium sulfate, filtering to remove the calcium sulfate, heating the resulting solution to drive off sulfur dioxide and to

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precipitate the manganese sulfites, calcining the sulfites to a manganese oxide, thereby driving off sulfur dioxide, and recycling the sulfur dioxide from the heating and calcining steps to the leaching step.

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