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PROCESS FOR TREATING MANGANESE ORES

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1 Claim. (Cl. 23—145)

My present invention relates to the treatment of manganese ores and particularly to a process for producing manganese dioxide from domestic manganese ores.

One of the chief uses for manganese at the present time is in the making of ferro-manganese or other manganese alloys such as silico-manganese and ferro-silico-manganese for use in steel making. Most of the manganese used today is produced by pyro-metallurgical operations from foreign manganese ores imported chiefly from Russia and Africa. These ores are high grade ores in that the Mn or MnO_2 content thereof is higher than that ordinarily found in the domestic manganese deposits which are widely distributed in the western part of the United States. These pyro-metallurgical operations are not carried out upon domestic manganese ores, mainly because of the lower Mn or MnO_2 content of such ores and also due to the fact that domestic manganese ores contain a number of other constituents which make the pyro-metallurgical operations either difficult or impractical. This inability to utilize domestic manganese ores is obviously a source of economic loss and hence a process which would enable simple and efficient treatment of domestic ores is very highly desired but insofar as I am aware there is no simple practical process known or available for this purpose.

It is accordingly one of the objects of my present invention to produce MnO_2 from domestic manganese ores in simple, inexpensive and efficient manner.

It is another object of my invention to produce MnO_2 from domestic manganese ores without especially resorting to pyro-metallurgical operations, thus eliminating the difficulties and expenses encountered in such operations.

It is a further object of my invention to produce MnO_2 from domestic manganese ores by simple physico-chemical operations which can be readily carried out without the need for any particular skill and which requires no expensive apparatus or equipment for its operation.

A still further object of my invention resides in dissolving in hydrochloric acid those fractions of the manganese ore which are soluble therein, in separating the solution from undissolved residues and then in selectively precipitating the manganese from the solution in the form of MnO_2 by a simple hydrolysis.

Other and further objects and advantages will be understood by those skilled in this art or will be apparent or pointed out hereinafter.

In carrying out the process of my present in-

vention I mine manganese ore in any suitable or approved manner and then grind or otherwise reduce the size of the same to a suitable extent. While the size to which the ore is reduced is not critical, I have found that in general the finer the state of subdivision the more rapid the subsequent treatment with hydrochloric acid becomes and by the same token this subsequent treatment dissolves a maximum percentage of the available values of the ore in a given period of time. For the above purposes I prefer to reduce the manganese ore to approximately 10-20 mesh, having the above explanation in mind, but I may reduce it to 60 mesh or finer if so desired.

After subdividing the ore to the desired mesh, I then roast the same for approximately 1 to 5 hours at a temperature within the range of approximately 500 to 750° C. This may be carried out in a rotary roaster of known type heated or fired in any known or approved fashion so long as the time interval of roasting and the temperature conditions meet the present requirements. This roasting not only acts to destroy organic matter and impurities which are burned off or volatilized under these conditions but the roasting operation causes a dehydrating action to occur and places the ore in particularly favorable form for the subsequent operations. The roasting may also be carried out in a muffle-furnace or other suitable stationary type furnace but in such case it is desirable to agitate or stir the material during the roasting operation to make sure of substantially uniform roasting of the ore.

The next step in my process is to treat the roasted ore with hydrochloric acid. Manganese ores usually consist primarily of manganese dioxide and silica but usually contain varying amounts of iron oxide and alumina with occasional small amounts of phosphorus and other impurities. A typical manganese ore from Utah contains approximately 40 to 70% MnO_2 with the balance mainly silica and a small percentage of iron oxide and alumina which usually run about 5 or 6% each and small percentages of phosphorus, etc. The phosphorus content may run from a trace up to a small percentage and there may be traces of other elements or compounds present.

The roasted ore is then treated or digested with hydrochloric acid, as above stated, until all the solubles pass into solution. The manganese dioxide, the iron oxide and alumina go into solution forming the respective chlorides MnCl_4 , FeCl_3 and AlCl_3 , but the silica and some of the other im-

purities remain undissolved. It is then only necessary to separate the residue from the solution by filtration and this may be carried out in any standard form of filter now known or used which is resistant to the action of hydrochloric acid.

In connection with this hydrochloric acid treatment there are certain considerations which should be noted at this point. For example, manganese is capable of forming at least two chlorides, one of which is designated by the formula $MnCl_2$ and the other of which is designated by the formula $MnCl_4$. In the present process it is my object to produce $MnCl_4$ to the greatest possible extent and I have found that this can be accomplished by utilizing concentrated hydrochloric acid which is relatively cold, that is, at room temperature or below. The use of cold concentrated hydrochloric acid distinctively favors the formation of $MnCl_4$. The amount of hydrochloric acid required for digestion can be readily determined by simple calculation based upon the particular analysis of the ore being treated and I add sufficient hydrochloric acid to convert all the manganese, iron and aluminum contents of the ore and any other chloride-forming constituents into their respective chlorides as above explained. While a small excess of hydrochloric acid is not particularly harmful, I prefer to add just enough acid to bring about the effects above set forth. The digestion takes place under atmospheric conditions and is usually complete in about $\frac{1}{4}$ -1 hour.

The residue which has been separated from the hydrochloric acid solution by filtration is thus separated out of the process and may be used for any desired purposes, such as for the production of refractories. The hydrochloric acid solution is next diluted with water which may be at room temperature or at the temperature at which it is discharged from the usual sources of water supply in the particular locality where the operations are being carried out. This dilution brings about a selective precipitation of MnO_2 by the hydrolysis of the $MnCl_4$ in accordance with the following reaction:



The MnO_2 formed by this hydrolysis in accordance with the just referred to equation precipitates out and appears in the solution as brick red particles which are of course hydrated. However, if the dilution has been carried out to the correct extent this precipitate, while initially rather fine, rapidly coalesces or coagulates into particles of appreciable size. I have found that this hydrolysis progresses quite rapidly after the addition of water for dilution and that hydrolysis is complete, that is the maximum MnO_2 precipitate is produced, in approximately 30 minutes. The iron chloride and aluminum chloride as well as any other chlorides which may be in solution do not change or become altered except of course they become more dilute but insofar as I am able to determine, MnO_2 alone selectively precipitates out during the hydrolytic action. The MnO_2 precipitate can then be filtered from the solution and to insure that it is as pure as possible it may be washed with water to eliminate solution adhering to the precipitate. The separated MnO_2 is then dried by a moderate heat and after this treatment is in granular form ready for use in making ferro-manganese or other manganese alloys for steel making purposes or for other uses in the arts.

Example

In one operation in accordance with the above process 10 grams of Utah manganese ore were roasted for $3\frac{1}{2}$ hours. This particular sample of ore had an MnO_2 content of approximately 70% and 44.3 grams of 35% HCl was used for dissolving purposes. The undissolved residue was filtered out and the filtrate was diluted to 400 ml. As the diluted solution stood it was apparent that a precipitate was gradually forming therein and that this precipitate was of red brown dark color and rather flocculent in condition. The precipitation and the coalescing or coagulating thereof appeared to be complete in about one-half hour and after this time the MnO_2 precipitate was filtered off, washed and dried and then appeared in granular condition with the typical appearance of MnO_2 .

In accordance with the above procedure I have been able to isolate the MnO_2 content of domestic manganese ores in a not only simple and novel manner but in a short space of time with a minimum of equipment and expense. The entire procedure from the grinding of the ore to the final production of the granular MnO_2 can be carried out in approximately five hours but where a longer roasting period is utilized the time will of course be that much longer. The simplicity and inexpensiveness of the foregoing procedure will be readily appreciated in comparison to expensive pyro-metallurgical operations requiring large and expensive equipment, the use of considerable power or fuel and the necessity for controlling temperatures and the like.

I have further discovered, however, that while a satisfactory yield or recovery can be secured in accordance with the above process this can be improved by following a somewhat modified procedure. By this I mean that since MnO_2 is soluble in hydrochloric acid and since the hydrolysis of $MnCl_4$ produces MnO_2 and HCl that in some cases it is advantageous to remove the HCl as it is formed by the hydrolytic action as this will better insure against any redissolving of a portion of the MnO_2 and this too is the reason for utilizing substantially the proper amount of acid necessary for dissolving and chloride forming operations as, if very much excess acid is used, the MnO_2 will have a tendency to partially dissolve in such excess acid. This modified process is the same as the above process up to the point where the solution or filtrate is separated from the undissolved residue. At this point in my modified process I heat the solution to a temperature where HCl will be evolved and as soon as the filtrate or solution reaches such temperature I add the water thereto in hot or boiling condition and continue to heat the whole while the hydrolytic action is going on. In this way not only is excess HCl eliminated from the solution but as the hydrolysis proceeds and hence as the hydrolysis reduces HCl as a by-product in accordance with the above-cited reaction this HCl is also evolved or driven away from the liquid. This hot hydrolysis, as I herein term it, has an additional advantage in that the heat produces a better precipitate of MnO_2 and at the same time enables recovery of the HCl by collecting the same and dissolving it in water, thus recovering it for re-use and keeping down the expense of the process. In connection with the preferred process, HCl is there recovered in the same manner after the MnO_2 has been removed by filtration.

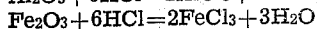
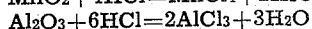
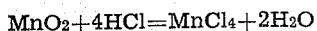
In some cases I also heat the ore and concen-

trated acid while the dissolving or digesting action is taking place. The temperature in this case need not exceed 150–200° F. but may range somewhat higher without deleterious effects.

5 This tends to lower the required time for the dissolving or digesting action and thereafter I may cool the same where the first described procedure is to be followed. Dilution should not take place until the hydrolysis, whether hot or cold, is to be effected.

10 My present invention therefore for the first time makes it possible to recover MnO₂ from any grade of manganese ore in a simple, inexpensive manner and in one which is free from the use of expensive equipment, the use of large quantities of power and the necessity for close control of any sort. With the foregoing description as a guide, anyone can produce pure MnO₂ from man-
15 ganeses ore cheaply and efficiently.

20 The above, however, is intended more in an illustrative than a limitative manner and so long as I adhere to the principles above set forth I may vary the same within the scope of the sub-joined claims. The precise amount of acid used will in any event depend upon the analysis of the
25 ore used at any given time and the main principle to be kept in mind in this connection is that dilution must be avoided until hydrolysis is ready to be effected. The amount of acid for the purposes of this invention can be readily determined from
30 the following typical reactions:



35 Where 35% HCl is utilized, the actual amount

of acid will of course be 100/35th of the amount required by the reactions and so on for other acid strengths. Thus in the above example, 7 grams of MnO₂ would require 11.76 grams of 100% HCl or 33.6 grams of 35% HCl. If I so desire I may
5 utilize chlorine gas or chlorine water in the manner and proportions which will be understood by those skilled in this art in view of the foregoing.

Having thus described my invention, what I claim as new and desire to secure by Letters Pat-
10 ent is:

A process for producing MnO₂ from manganese or which comprises pulverizing manganese ore as mined to a relatively fine state of subdivision, roasting the pulverized ore for one to five hours
15 at a temperature within the range of about 500–750° C. to destroy organic impurities, to dehydrate the ore and to put it in condition for further treatment, adding sufficient cold concentrated hydrochloric acid to the roasted ore to con-
20 vert the manganese content thereof to MnCl₂ and other chloride-forming constituents to their respective chlorides, digesting the ore in the acid for about ¼ to 1 hour under prevailing atmos-
25 pheric conditions, filtering out insolubles, diluting the filtrate with water to about ten times its volume to precipitate MnO₂ selectively from the diluted filtrate, letting the same stand for about ½ hour to produce maximum hydrolytic
30 precipitate and to coagulate and coalesce the initially fine precipitate, filtering off the MnO₂ precipitate, washing it and finally drying it at moderate temperature to produce a substantially pure granular MnO₂.

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CERTIFICATE OF CORRECTION.

Patent No. 2,154,128.

April 11, 1939.

ALBERT L. JACOBS.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 2, second column, line 63, for the word "reduces" read produces; 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 13th day of June, A. D. 1939.

Henry Van Arsdale

(Seal)

Acting Commissioner of Patents.