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ART OF RECOVERING MANGANESE DIOXIDE
FROM PSILOMELANE

Albert L. Jacobs, Pittsburgh, Pa.

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My present invention relates to the recovery of manganese values from manganese ores and is more especially concerned with the recovery of manganese dioxide from psilomelane, which is a manganese ore found in the United States and other parts of the world and which contains manganese dioxide in a colloidal condition.

Manganese is a strategically important metal, particularly in connection with steel-making operations. It is used not only for scavenging and deoxidizing purposes but also for actual alloying with steel to produce compositions having special properties. This manganese is generally employed as ferro-manganese. Ferro-manganese, in turn, is generally produced by smelting manganese dioxide with a suitable reducing agent such as carbon, aluminum or silicon in the presence of iron to produce a Fe-Mn alloy, which is the active agent employed for steel making purposes.

While some deposits of manganese ores exist in the United States, they are neither abundant nor high grade and, therefore, manganese has been largely an imported commodity. Apparently the domestic manganese ores have not been exploited for the production of manganese oxide and/or ferro-manganese due to their comparatively poor grade and more especially due to a lack of a commercial procedure. Smelting procedures have been found not to be practicable in connection with low grade domestic manganese ores.

It is one of the objects of the present invention to make possible the production of manganese oxide from that ore known as psilomelane.

Another object of the invention resides in a simple procedure based upon logical chemical principles which will enable the production of manganese oxide from manganese ores occurring in the United States.

A further and more specific object of the invention resides in producing MnO_2 from a domestic manganese ore while avoiding smelting procedures or pyro-metallurgical operations in general, it being an accepted fact that domestic manganese ores do not lend themselves to handling by such older types of procedure.

Other and further objects and advantages will be understood from what follows or will be appreciated by those skilled in this field.

Psilomelane is composed essentially of manganese dioxide, iron oxides, silica and water both in the form of moisture and as combined water of constitution. The manganese dioxide

content of psilomelane varies, but in a particular deposit in the State of Pennsylvania this runs in the neighborhood of 70-72%. The silica and iron oxides together are in the neighborhood of 20% and the water constitutes the balance. One particular analysis runs approximately 71.74% MnO_2 , 20.68% silica and iron oxides, 6.80% combined water and 0.78% moisture. In some cases psilomelane contains sodium, barium and other alkalies and alkaline earth salts, and in all cases is contaminated with dirt, clay and other extraneous matter. The ore is, however, hard, brittle and of comparatively high specific gravity, a fracture having a lava-like appearance frequently with definite stratification and flow lines visible. It occurs in botryoid form, either massive or stalactitic. As its name indicates, the ore is usually characterized by a black appearance and smooth surfaces. Ordinarily it contains a reddish coating of iron oxide, and its surface irregularities are frequently filled with dirt, clay, etc.

In accordance with the present invention, the psilomelane is mined in any suitable manner, it occurring in the instance above noted only a few feet below the surface and overlain with a stratum of clay. This clay is stripped off and the underlying psilomelane can be removed by blasting and steam shovel operations. The particular manner of mining the same forms per se no essential part of this invention. After mining, the psilomelane is then crushed to a suitable state of subdivision, preferably anywhere from 20 to 100 mesh. In general, the finer the state of subdivision the better for subsequent operations and the less time required for further treatment. The invention is, however, capable of acting upon the ore regardless of its particular state of subdivision. While general uniformity of particle size is advantageous, this too is not a restriction upon the effectiveness of the present method. Any suitable apparatus may be employed for the crushing operation such as a jaw-type crusher or a grinding mill.

The psilomelane as thus mined and crushed is next subjected to a mild roasting operation. The purpose of this is to eliminate organic matter and to exert a dehumidifying effect which places the material in a favorable state for the acid treatment which follows. The temperature of this roasting operation need not exceed a temperature which will effect a destruction of the organic matter and a driving off of water. For example, this roasting procedure may be carried out in the neighborhood of about 250-

600° F., and while it may exceed this temperature a higher heat is usually not required. The driving off and/or breaking down of water which occurs during the roasting operation has the further effect of "demineralizing" the ore and, in other words, the colloidal manganese dioxide is released from the mineral compounds which hold the particles together as a rocky mass. The time factor involved in the heating need only be such as to effect the purposes noted and, in general, the roasting temperature need not be maintained for more than a relatively brief period of the order of one-half hour to one and one-half hours. Prolonged heating has no proportionate effect which would justify the additional expense. Shorter heating can be employed in some cases provided it is long enough to ensure that all parts of the material reach the required temperature. The roasting operation may be carried out in conventional equipment such as is now used, e. g. in a roaster of the rotary type, externally fired, and provision should preferably be made for preventing the temperature from very much exceeding the ranges noted.

The roasted ore is now subjected to digestion with hydrochloric acid. Knowing the approximate manganese dioxide and iron oxide contents of the ores—or determining such in a given case by suitable analysis—sufficient hydrochloric acid is added to effect conversion of these two components of the ore to chlorides in solution. The concentration of acid which is used should be that which produces maximum rate of dissolution; other than this, the acid concentration may be varied. Dilute acid of conventional commercial strengths may be used with entire satisfaction. The digestion should take place in a suitable tank of adequate capacity, and preferably agitation should be carried out during the dissolving action as this presents a greater surface of material to the acid and thus expedites the formation of the chlorides in solution. Preferably, a slight excess of acid should be employed not only to ensure complete solution of the manganese and iron contents of the ore but also to maintain the solution pressures in the desired direction of reactivity while preventing the reaching of undesirable equilibria or static conditions at which the rate of solution is slow. Ordinarily a period ranging from about 10 to 60 minutes will be ample for dissolving the entire manganese and iron contents of the ore. The time here is related to the fineness of subdivision, the acid strength and the temperature. The tank and the agitator when employed should, of course, be suitably protected against corrosion from the acid used as the solvent, and in this connection the material known to the trade as "Duriron" may be employed satisfactorily. The digestion may take place at room temperature; warming, however, increases the rate of chloride formation.

After the completion of the dissolving and digesting actions it will be found that there is a certain proportion of the ore which remains undissolved. This is composed chiefly of silica, which is not attacked by the hydrochloric acid, and also of other extraneous materials in the nature of gangue. The solution is next separated from the undissolved residue. This may be effected by settling, followed by decantation or siphoning, but I prefer to pump the solution through a suitable filter press not only because this usually provides a better or sharper separation of the solution from the solids but because

the rate of separation is generally more rapid. Any suitable filter press may be employed and the same is, of course, protected against attack from the hydrochloric acid, as will be appreciated. The filter cakes will be composed of substantially pure silica, which may be employed for refractory or other purposes, and constitutes a valuable by-product.

The clear filtrate is composed substantially only of manganese and iron chlorides together with some excess of hydrochloric acid where an excess has been employed. The procedure is then to separate the manganese and the iron from each other and to place the manganese in useful form. This may be accomplished in at least two ways, which are hereinbelow explained.

One mode of procedure involves the precipitation of the iron as Prussian blue in the manner set forth in my copending application Serial No. 139,968. The pertinent portions of that application are hereby made a part hereof. Such procedure involves the addition of potassium ferrocyanide to the acid solution of manganese and iron chlorides with the resultant formation of a Prussian blue precipitate $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$. This blue precipitate is next removed from the reaction mixture by filtration of any approved kind and the same isolated in such way. For the sake of economy—for strategic and war purposes the matter of economy is not of primary importance—the Prussian blue is then separately treated with potassium hydroxide to effect the reaction set forth in my aforesaid copending application, this converting the Prussian blue precipitate back to potassium ferrocyanide, which may be recovered and reused as will be understood, and leaving the iron content of the ore in the form of iron hydroxide, which, if desired, may be heat-converted to iron oxide.

After removal of the blue precipitate the solution then consists substantially entirely of manganese—and some potassium—compounds in solution and these may be recovered as hereinafter provided. The solution of manganese may be subjected to evaporation either by the direct application of heat alone or by the conjoint action of heat and reduced pressure, the same being carried on until the chloride is broken down and the chlorine content driven off. This may itself be recovered for regenerating hydrochloric acid and, therefore, for reuse in the procedure, thus further adding to the economies thereof. Ultimately the manganese becomes converted to manganese dioxide by taking up oxygen from the air. The MnO_2 is next isolated from the water-soluble potassium, etc. compounds and this can be readily done by a simple washing or leaching operation. The MnO_2 thus produced is in condition for use.

The manganese and iron chloride solution may be treated to recover manganese dioxide in another manner which forms a modified form of this invention. This is utilized subsequent to the iron removal procedure and instead of the evaporation and leaching steps. By this optional procedure the iron-free manganese chloride solution is diluted until manganese dioxide is precipitated as such by selective hydrolysis in accordance with my issued Patent No. 2,154,123. This procedure is applicable particularly in those cases where a concentrated or relatively concentrated hydrochloric acid has been employed and no heat utilized and thus where the conditions have favored the production of manganese tetrachloride (MnCl_4) in solution rather than the lower man-

ganese chlorides such as $MnCl_2$ and/or $MnCl_3$. The desiderata governing this will be understood from a reference to my aforesaid patent.

Reverting to the solution of manganese and iron chlorides produced after separation from silica, etc., I may proceed as to such in a direct manner to separate the manganese from the iron. This procedure involves the immediate application of the selective hydrolysis principles referred to above and set forth in my aforesaid patent without employing the intermediate iron-removal procedure interposed in accordance with my aforesaid copending application. Therefore, in this modification of the invention the initial chloride solution is produced under such conditions as to favor the production of $MnCl_4$ as already pointed out. The selective precipitation is effected by mere dilution, which has no action upon the iron chlorides (except an innocuous dilution) which remain in solution. Should it be desired to recover the iron values, this can readily be accomplished either by evaporating the solution to dryness and recovering iron chloride as such, or heat may be applied as already described to break down the iron chloride, recovering the chlorine for the regeneration of hydrochloric acid for reuse in the procedure and converting the iron to iron oxide, which forms a valuable constituent of paint, rouge and other commercial products.

It will therefore be appreciated that in accordance with the principles of the present invention MnO_2 may be simply, readily and, if so desired, economically produced from psilomelane and other manganese dioxide-bearing ores wherever the present principles and procedure apply. The subsequent procedure of producing ferro-manganese per se forms no essential part of this invention. The MnO_2 produced is substantially chemically pure, depending upon the care with which the procedure is carried out. The MnO_2 is in a granular form and is preferably subjected to a final washing and drying operation, which latter may be a mild heating. In producing MnO_2 by means of the selective hydrolysis principle, I have discovered, as set forth in my said patent, that a better precipitate is secured by allowing a certain waiting period of approximately 30 minutes between the time when the precipitate first appears and its separation from the residual materials. Particularly in stronger acid solutions, however, the precipitate has a good character and presents no difficult filtration problem. While I have above referred to evaporating the chloride solutions by heat with or without reduced pressure, it is to be understood that any of the described solutions which are to be reduced to a dry or solid condition may be so produced by spray drying operations. These, per se, are well known in the production of powdered milk, for example, and therefore need not be described in detail. The solution impinges on a rapidly rotating disc which discharges it centrifugally in the form of a spray or atomized particles which fall through a chamber in which their water is removed by a warm or hot updraft. There is a direct production of powder from the solution therefore. Such is a definite part of my invention. I may also employ some other chloride or chlorine compound in place of HCl and in some instances chlorine water may be so employed. Other additions, omissions, substitutions and modifications may be made without departing from the spirit and scope hereof.

Rather the invention is that defined by the appended claims.

Having thus described my invention, what I claim as new and desire to secure by Letters Patent is:

1. Process for producing MnO_2 from a manganese ore such as psilomelane which contains manganese dioxide and oxides of iron and silicon comprising roasting the manganese ore, adding sufficient hydrochloric acid to convert the manganese and iron contents of the ore to a solution of their respective chlorides, removing insolubles, eliminating iron from the chloride solution and recovering MnO_2 from the balance of the solution by evaporation and ignition followed by leaching.

2. Process for producing MnO_2 from a manganese ore such as psilomelane which contains manganese dioxide and oxides of iron and silicon comprising roasting the manganese ore, adding sufficient hydrochloric acid to convert the manganese and iron contents of the ore to a solution of their respective chlorides, removing insolubles, eliminating iron from the chloride solution and recovering MnO_2 from the balance of the solution, the iron elimination including the addition of potassium ferrocyanide to the solution, the removal of the blue precipitate thus formed and the regeneration of the potassium ferrocyanide by adding KOH to the isolated blue precipitate and the removal of the thus formed iron hydroxide therefrom.

3. Process for producing MnO_2 from a manganese ore such as psilomelane which contains manganese dioxide and oxides of iron and silicon comprising roasting the manganese ore, adding sufficient hydrochloric acid to convert the manganese and iron contents of the ore to a solution of their respective chlorides, removing insolubles, eliminating iron from the chloride solution and recovering MnO_2 from the balance of the solution by evaporation and ignition followed by leaching, the iron elimination including the addition of potassium ferrocyanide to the solution, the removal of the blue precipitate thus formed and the regeneration of the potassium ferrocyanide by adding KOH to the isolated blue precipitate and the removal of the thus formed iron hydroxide therefrom.

4. Process for producing MnO_2 from a manganese ore such as psilomelane which contains manganese dioxide and oxides of iron and silicon comprising roasting the manganese ore, adding sufficient hydrochloric acid to convert the manganese and iron contents of the ore to a solution of their respective chlorides, removing insolubles, eliminating iron from the chloride solution and recovering MnO_2 from the balance of the solution by selective hydrolysis, the iron elimination including the addition of potassium ferrocyanide to the solution, the removal of the blue precipitate thus formed and the regeneration of the potassium ferrocyanide by adding KOH to the isolated blue precipitate and the removal of the thus formed iron hydroxide therefrom.

5. Process for producing MnO_2 from a manganese ore such as psilomelane which contains manganese dioxide and oxides of iron and silicon comprising roasting the manganese ore, adding sufficient hydrochloric acid to convert the manganese and iron contents of the ore to a solution of their respective chlorides, removing ore components insoluble in hydrochloric acid, precipitating iron in the form of Prussian blue, separating the Prussian blue to produce a solution con-

taining the manganese of the ore, evaporating the solution to dryness, driving off volatiles, leaching the solid thus produced and recovering manganese therefrom as MnO_2 .

6. Process for producing MnO_2 from a manganese ore such as psilomelane which contains manganese dioxide and oxides of iron and silicon comprising roasting the manganese ore at a temperature within the range of about 250-600° F. for a short period of time of the order of $\frac{1}{2}$ -1½ hours, adding sufficient hydrochloric acid to con-

vert the manganese and iron contents of the ore to a solution of their respective chlorides, removing ore components insoluble in hydrochloric acid, precipitating iron in the form of Prussian blue, separating the Prussian blue to produce a solution containing the manganese of the ore, evaporating the solution to dryness at reduced pressure, continuing the heating of the solid formed by the evaporation and leaching such solid with water to remove solubles and to leave MnO_2 as the residue.

ALBERT L. JACOBS.