UNITED STATES PATENT OFFICE.

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PROCESS OF EXTRACTING VALUES FROM MANGANESE AND OTHER ORES.

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To all whom it may concern:

Be it known that we, EDWARD W. HASLUP and BENJAMIN A. PEACOCK, both citizens of the United States, respectively residing at Bronxville, Westchester county, New York, and Philadelphia, Philadelphia county, Pennsylvania, have invented certain new and useful Improvements in Processes of Extracting Values from Manganese and other Ores; and we do hereby declare the following to be a full, clear, and exact description of the invention, such as will enable others skilled in the art to which it appertains to make and use the same.

This invention relates to a process of extracting manganese from its lean ores and has for its object to provide a process which will be more efficient and less costly than those heretofore proposed.

With these and other objects in view the invention consists in the novel steps and combinations of steps constituting the process, all as will be more fully hereinafter disclosed and particularly pointed out in the claims.

In order that the precise invention may be the more clearly understood it is said:—As is well known, manganese often occurs in ores or minerals in such small quantities, or in such a physical condition that the usual methods of extraction, involving the action of gravity, are either substantially impracticable, or they require such an extensive treatment with such a costly plant and appliances, that they are commercial failures under normal conditions of costs.

Likewise processes employing sulfuric acid or other acids have frequently failed due to the low content of the manganese in the ores, to the comparatively low temperature at which, or to the comparatively short time during which the acid has acted, to the fact that it was not practicable to prevent the acid from attacking the containing vessel, or to a combination of these causes.

On the other hand, there are many lean manganese deposits, often in the form of sands, or clays, in which a large proportion of the manganese is present as a hydrous oxid, a silicate, etc., and in which a crystalline structure has substantially disappeared. These deposits offer an attractive field for an acid process such as that disclosed below in which the above objections are avoided.

Further, these ores contain in addition to their tenor of manganese, more or less combined potassium and aluminum, and also frequently some zinc, nickel, cobalt, copper, tungsten, and other substances of a greater or less commercial value when the process employed is capable of economical recovering the same. The mineral psilomelane is a familiar example of an ore suitable for the right kind of an acid process in that it is a hydrous manganese-manganate in which a part of the manganese has been replaced by barium or potassium, so that it varies in composition, is generally more or less impure and rather lean in values, so, in many cases it cannot be commercially worked by acid processes heretofore proposed, while it readily lends itself to the acid process to be disclosed below. In chemical characters this said mineral may be written as $MnO_2.(Mn, K,Ba)O.nH_2O$. The material known as "wad" is also an important ore of manganese suitable for a proper acid process that is not too costly. It occurs in amorphous and reniform masses either earthy, or compact. It is usually very soft and often loosely aggregated. It is probably a more or less alterated product of pyrolusite, psilomelane and other minerals, and is frequently too poor in values to warrant acid processes heretofore known.

Further, the gangues of manganese ore bodies are frequently more or less micaceous and therefore, the successful recovery of any alteration products resulting from the decomposition of these said gangues by an acid will materially add to the value of the combined potassium recovered, while the successful recovery of the other compounds of a greater or less commercial importance will lessen the cost of treating the original manganese bearing material if a proper acid process is employed.

When manganese dioxid MnO_2, as well as most of the other compounds of manganese, are treated with strong sulfuric acid at temperatures above 100° C. substantially all the manganese present goes into solution, with the formation of manganese sulfates. At the same time, substantially all the alkali metals present, more or less of the aluminum, copper, zinc, etc., present also form sulfates. But when dealing with lean ores, unless the objections above mentioned to the prior acid processes can be overcome, these desirable features and reactions cannot be

utilized in a commercial acid process, for too much acid will be required to recover too small a quantity of manganese.

One way of overcoming these objections has been to employ only hand picked or refined ores comparatively rich in manganese; but the hand picked, as well as the refined manganese ores of commerce do not have any considerable mineral content other than the manganese itself, and therefore, the ores of a low manganese content, and those offering the above mentioned physical objections cannot be thus utilized. On the other hand, the raw ores, at times, before picking, contain as much as say seven per cent. of potassium oxid K_2O, two per cent. copper-oxids, and three per cent. oxid of tungsten, much of which values can be saved by the process now to be disclosed.

We have discovered that we may take the ordinary run of the mined manganese ores, although they are comparatively lean in manganese, grind them to say forty or fifty mesh, and then mix the mass thus produced with sulfuric acid of say about 50° Bé., or as high as 55° Bé. The resulting mixture of magma is next discharged into a closed receptacle or "den" where it is held for say twenty four to forty eight hours, and protected from rapid cooling by the thick non-metallic, non-heat-conducting walls of the "den" or by other means. The quantity of acid employed is somewhat in excess of that required to convert to sulfates those constituents present that it is desired to recover in a soluble form, but not sufficient to convert the iron and other valueless constituents present. Owing to the conservation of the heat evolved inside the "den" and to the time the acid is allowed to react, as well as to the regulated quantity of acid employed, the said acid acts substantially completely and with the greatest economy on the desired values. It also acts, in a sense selectively, since owing to its limited quantity it attacks the most reactive metals first and the least reactive last, and the latter in a minimum quantity.

In this way, we are enabled to convert to sulfates substantially all the manganese present, as well as the potassium and other basic components of the gangue, even though all these constituents of the ore are in rather lean proportions. At the same time, no considerable proportion of the iron oxid present is attacked, the latter remains with the insoluble residue, and acid that would otherwise be wasted is saved.

It will thus be seen that an important feature of this process resides in utilizing the chemical heat generated over a long period of time to raise the mass to the reacting temperature. The receptacle being closed and provided with heat insulating, as well as acid resisting walls, the heat is conserved, is allowed to accumulate while new reactions start, which generate more heat and thus the acid is used up in a most economical manner at the proper temperatures to insure a recovery of the most important values and without being wasted in attacking the walls of the vessel, or in decomposing worthless compounds present. In fact, the temperature often rises in the mass to a point between 200° C. and 300° C., which greatly promotes the attack by the acid of valuable constituents which in other acid processes would be lost, unless a much greater quantity of acid is employed.

After the desired valuable constituents of the ore have been thus converted into crude sulfates, the latter are extracted with water, and the values in the solution thus obtained are recovered by any suitable well known methods, such as concentration, and fractionation, or by precipitation and fractionation.

It is an especially important feature of this invention that no water is added to the ore, the effect of which would be to waste the acid and lower the internal temperature of the mass. It is also important after the acid has dissolved all the values it will dissolve in any case at relatively low temperatures, that the heats of reaction are conserved and thus caused to raise the silicates present to temperatures at which they will decompose and their values be attacked by the acid.

Stated in other language, if heat were supplied from the outside, before the necessary temperature for the decomposition of the silicates was reached, a considerable portion of the acid would be volatilized, while no such loss is experienced by proceeding as above disclosed. It therefore follows that by employing an acid of a sufficiently low specific gravity to permit a ready permeation of the mass, by employing it in quantities insufficient to attack all the iron present, but somewhat in excess of that sufficient to attack the other and desired values present, by preventing the heats of reaction from escaping from the receptacle or "den" as by making the walls of the latter of non-metallic, non-heat conducting material, and by keeping the receptacle closed for say twenty four hours or forty eight hours to permit all the acid to be used up, we are enabled to form soluble sulfates of the values in the ore with a substantially less quantity of acid than has been heretofore possible, while at the same time, we are enabled to recover a maximum of different values with a single charge of acid, and thus to partially pay the costs of the process by said last named values. In fact, by the process disclosed, we are enabled to work lean manganese and other ores containing a plurality of values, no one of which is

present in a quantity sufficient to warrant working, but the aggregate of which make up a richness which will pay for working the process disclosed.

It is obvious that this process is not confined to the recovery of manganese from its ores, nor to the use of sulfuric acid, for it may be applied to other minerals and with other acids. Therefore, we do not wish to be limited to the above disclosure except as may be required by the claims.

What we claim is:—

1. The process of extracting values capable of being leached with sulfuric acid from their ores which consists in finely dividing said ores; mixing the finely divided material with acid; transferring the mixed ore and acid to a closed receptacle from which a substantial portion of the heat of reaction is prevented from escaping; holding the reacting mass in said receptacle for more than ten hours; extracting the reaction products from the mixture; and recovering the desired values from said products, substantially as described.

2. The process of extracting values capable of being leached with sulfuric acid from their ores which consists in finely dividing said ores; mixing the finely divided material with sulfuric acid; transferring the mixed ore and acid to a closed receptacle from which a substantial portion of the heat of reaction is prevented from escaping; holding the reacting mass in said receptacle for more than twenty hours; extracting with water the reaction products from the mixture; and recovering the desired values from said products, substantially as described.

3. The process of recovering manganese values from ores which consists in finely dividing said ores; mixing the same devoid of added water with a measured quantity of sulfuric acid; confining the mixed ore and acid in a closed receptacle until the accumulated heat of reaction has caused substantially all the manganese present to be converted into the form of sulfates; extracting said sulfates with water; and recovering the manganese values from the solution thus obtained, substantially as described.

4. The process of recovering manganese and other values capable of being attacked by sulfuric acid from ores which consists in finely dividing said ores; mixing the same devoid of added water with sulfuric acid; confining the mixed ore and acid in a closed receptacle from which the heats of reaction have been prevented from escaping, until the accumulated heat of reaction has caused substantially all the manganese and other desired values present to be converted into the form of sulfates; extracting said sulfates with water; and recovering the manganese and other values from the solution thus obtained, substantially as described.

5. The process of recovering manganese and other values capable of being attacked by sulfuric acid from ores which consists in finely dividing said ores; mixing the same with sulfuric acid; confining the said ore devoid of added water and said acid in a closed receptacle until the accumulated heat of reaction has raised the temperature of the mass above 100° C. and substantially all the manganese and other desired values present have been converted into the form of sulfates; extracting said sulfates; and recovering the manganese values from the solution thus obtained, substantially as described.

6. The process of recovering manganese and other values capable of being attacked by sulfuric acid from ores which consists in finely dividing said ores; mixing the same with sulfuric acid of a gravity not more than 55° Bé.; confining the said ore devoid of added water and said acid in a closed receptacle until the accumulated heat of reaction has raised the temperature of the mass above 150° C. and substantially all the manganese and other desired values present have been converted into the form of sulfates; extracting said sulfates; and recovering the manganese values from the solution thus obtained, substantially as described.

7. The process of recovering values capable of being attacked by sulfuric acid from ores which consists in mixing ore devoid of added water in a finely divided state with sulfuric acid in a limited quantity, and not substantially exceeding 55° Bé.; causing the heats of reaction to gradually raise the internal temperature of the mass above 100° C.; and extracting with water the soluble sulfates thus formed, substantially as described.

8. The process of recovering a plurality of values capable of being attacked by sulfuric acid from ores too lean in any single value to warrant working, which consists in mixing said ores in a finely divided state and devoid of added water with sulfuric acid in a quantity sufficient to convert the desired values but insufficient to convert the other constituents; causing the heats of reaction to raise the mixture to temperatures at which the desired reactions will take place; extracting with water the desired values; and separating out each value from the crude solution thus obtained, substantially as described.

In testimony whereof we affix our signatures.

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