UNITED STATES PATENT OFFICE.

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PROCESS OF EXTRACTING MANGANESE FROM LEAN ORES.

1,279,108. Specification of Letters Patent. Patented Sept. 17, 1918.

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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, residing, respectively, at Bronxville, Westchester county, New York, and Philadelphia, Philadelphia county, Pennsylvania, have invented certain new and useful Improvements in Processes of Extracting Manganese from Lean 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 improve the methods heretofore proposed.

With this 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.

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 vessels, 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 zinc, nickel, cobalt, copper, tungsten, and other substances of a greater or less commercial value when the process employed is capable of economically 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 cannot be worked by many processes, 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.

Further, the gangues of manganese ore bodies are frequently more or less micaceous and therefore, alteration products resulting from decomposition of these said gangues by an acid, materially add the value of the combined potassium recovered and of other compounds of a greater or less commercial importance to the value of the original manganese bearing material. 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, as well as more or less of the aluminum, copper, zinc, etc., present also form sulfates. But unless the objections above mentioned to the prior acid processes can be overcome, these desirable features cannot be utilized in a commercial acid process. One way of overcoming these objections has been to employ only hand picked or refined manganese ores, but the hand picked, as well as the refined manganese ores of commerce do not have any considerable mineral content other than manganese, and therefore the ores of a low manganese content, and many offering physical objections cannot be utilized for a hand picked or other prior process. On the other hand, the raw ores, at times, may contain as much as seven per cent. of potassium oxid K_2O, two per cent. copper oxids, and three per cent. oxid of tungsten, much of which can be saved by the process now to be disclosed.

In carrying out this invention we may, for example, take the ordinary run of mined manganese ores, which may be too lean in manganese to be capable of commercial working by prior processes, and add predetermined quantities of other ores, to be disclosed below, whereupon we grind the mixture to say 50 mesh, and without any addition of water to the finely divided material we then add sufficient sulfuric acid in excess to convert to the sulfates all the values it is desired to extract, but not sufficient to convert the iron present. The resulting mixture or magma is next discharged into a closed receptacle or "den" where it is held for say 24 to 48 hours, and protected from rapid cooling by the thick non-metallic non-heat-conducting walls of the den or by other means. Owing to the conservation of the heat evolved 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.

It also acts, in a sense selectively, because owing to its limited quantity it attacks the most reactive metals first and the least reactive last, and the latter in a minimum of quantity.

In this way we are enabled to convert to sulfates substantially all the manganese present in the mixed ores, even though these constituents of the ore are in proportions too lean to be commercially worked by prior processes. At the same time no considerable proportion of the iron oxid present being attacked, the latter remains with the insoluble residue.

After the desired constituents of the mixed ores have been 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 by concentration and fractionation, or by precipitation and fractionation.

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, 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. 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 constituents which in other acid processes would be lost.

Another important feature of this invention resides in the fact that substantially no water is added to the ore. The absence of added free water in the mass enables the sulfuric acid to raise the latter to a higher temperature, and therefore to attack with greater vigor the more electro positive metals present in a combined state. The heat thus generated immediately raises those combined metals which are less electro-positive to a reacting temperature, and the heat generated from the attack on said last mentioned metals serves to still further raise the temperature of the mass, with the result that the reaction proceeds to a completion with an amount of acid which would be impossible if an ordinary autoclave form of vessel were employed, or if added free water or other dilutents were present. This principle becomes important when it is remembered that the artificial heating of the mass would not accomplish the same purpose, because sulfuric acid under such heating would be volatilized, and would fail to completely decompose the less electro positive metal compounds.

In very lean manganese ores such as are contemplated by this process, there is generally present an insufficient quantity of the more electro positive bases, such as manganese, potassium, etc., to liberate the necessary heat to raise the mass up to a temperature at which the less electro positive compounds would be attacked, and, therefore, the reaction or process will fail to be commercial unless this defect is avoided. In such cases we add an ore containing a compound which is readily attacked by sulfuric acid at ordinary temperatures and also yields a valuable by product, and we thus raise the temperature to a point sufficiently high for the other constituents to be attacked, while at the same time obtaining a by-product of a value sufficient to make the process commercially successful.

That is to say, suppose, for example, the manganese should be present in the ore, in quantities of only about three per cent. or four per cent., and suppose the potassium should be present in like small quantities. Then no matter how high one may heat the mass artificially the reaction would not be a commercial success.

In such cases we purposely add to the charge an ore carrying a compound in a quantity sufficient when converted into a sulfate to not only produce a valuable by product but to also produce the desired quantity of heat. Such an ore is serpentine, or a similar silicate, containing a relatively large proportion of magnesium. Or we may add the mineral known as pyrophyllite having a composition of say $H_2Al_2(SiO_3)_4$, which forms with the sulfuric acid an aluminum sulfate also constituting a valuable by-product.

In either case, a very considerable quantity of heat is at once liberated, and this heat serves to raise the temperature of the surrounding mass sufficiently for the reaction to proceed. As a specific example of the carrying out of this process, we may take a well known manganiferous clay found in the State of Virginia, and which may be said to have a composition varying substantially as follows:—

	Sample No. 1.	Sample No. 2.
	Per cent.	*Per cent.*
H_2O	11	11
M_nO_2	11	6
Fe_2O_3	6	7
K_2O	5	2
Al_2O_3	30	41
SiO_2	34	40
BaO	1	1
CaO	1	1
MgO	1	1
	100	100

After finely subdividing the said clay of sample #1, we add sufficient sulfuric acid, slightly in excess, to unite with all of the MnO_2, the K_2O, the CaO and the MgO present, but not enough to unite with the iron, the aluminum or other constitutents present. In the case of a clay having as much manganese and potassium as is indicated in said sample #1, the addition of very little, if any serpentine, or other mineral, will be found necessary, but a little serpentine will greatly improve the process. In such cases, after the mass has been confined for a period of say 24 to 48 hours, the crude sulfates of manganese, potassium and magnesium are readily separated out and recovered in the manner stated. On the other hand, when the manganese or the potassium are not present in sufficient proportions as is the case in sample #2, we may then add any suitable quantities of serpentine, or other minerals, which contain constituents that are readily attacked by the sulfuric acid and which provide valuable by-products, and we proceed in the manner above disclosed.

The quantity of serpentine or other minerals added will in each case depend upon the leanness of the manganese ore, the quality of the serpentine, and the amount of by-product it is desired to produce. But, in so far as maintaining the reaction is concerned, any quantity may be added which will bring the total quantities of manganese and magnesium in the charge above say 10 per cent. or 15 per cent. In our copending application #200,813, filed Nov. 7, 1917, entitled Process of extracting values from manganese and other ores, we have disclosed and claimed a process similar to the one above outlined, except no addition of serpentine or other similar ores is contemplated.

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 from lean ores capable of being leached with sulfuric acid which consists in finely dividing said ores; adding to said ores in a finely divided state other minerals containing a constituent which is capable of reacting exothermically in the process; mixing the finely divided ore material devoid of added free water with an acid; transferring the mixed ore and acid to a closed receptacle also devoid of added free water, and from which a substantial portion of the heat of reaction is prevented from escaping; holding the reacting mass in said receptacle for a period of more than fifteen hours; extracting the reaction products from the residue; and recovering the desired values from said products, substantially as described.

2. The process of extracting values from lean ores capable of being leached with sulfuric acid which consists in finely dividing said ores; adding to said ores in a finely divided state other minerals containing a constituent which is capable of reacting exothermically in the process; mixing the finely divided ore 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 a period of more than twenty hours; extracting with water the reaction products from the residue; and recovering the desired values from said products, substantially as described.

3. The process of recovering manganese values from lean ores which consists in adding to said ores other minerals containing a constituent that is capable of reacting exothermically with sulfuric acid; finely dividing said mixed ores; mixing the finely divided ore material with a limited quantity of sulfuric acid; transferring said ore devoid of added water and mixed with said acid to a closed container from which a substantial portion of the heat of reaction is prevented from escaping; confining the mass in said container until the accumulated heat 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 from lean manganiferous ores which consists in adding other minerals containing a constituent capable of reacting exothermically with sulfuric acid; finely dividing the mixture thus produced; adding a limited quantity of sulfuric acid to the finely divided material; confining the mass for more than twenty four hours in a closed receptacle from which the heat of reaction is prevented from escaping; extracting the resulting sulfates with water; and recovering desired values from the solution thus obtained, substantially as described.

5. The process of recovering manganese and other values from lean ores which consists in adding another mineral containing combined potassium to said ores; finely dividing the mixture; adding sulfuric acid in a limited quantity to the finely divided ore; confining the ore devoid of added free water mixed with said acid in a closed receptacle from which the heat of reaction is prevented from escaping until the desired values have been transformed into sulfates; extracting said sulfates with water; and recovering said values from the solution thus obtained, substantially as described.

6. The process of recovering manganese and other values from lean ores which consists in adding another mineral containing combined potassium to said ores; finely dividing the mixture; adding sulfuric acid of a gravity not more than 55° Bé., in a limited quantity to the finely divided ore; confining the ore devoid of added free water mixed with said acid in a closed receptacle from which the heat of reaction is prevented from escaping until a temperature above 150° C. is reached and until the desired values have been transformed into sulfates; extracting said sulfates with water; and recovering said values from the solution thus obtained, substantially as described.

In testimony whereof we affix our signatures.

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