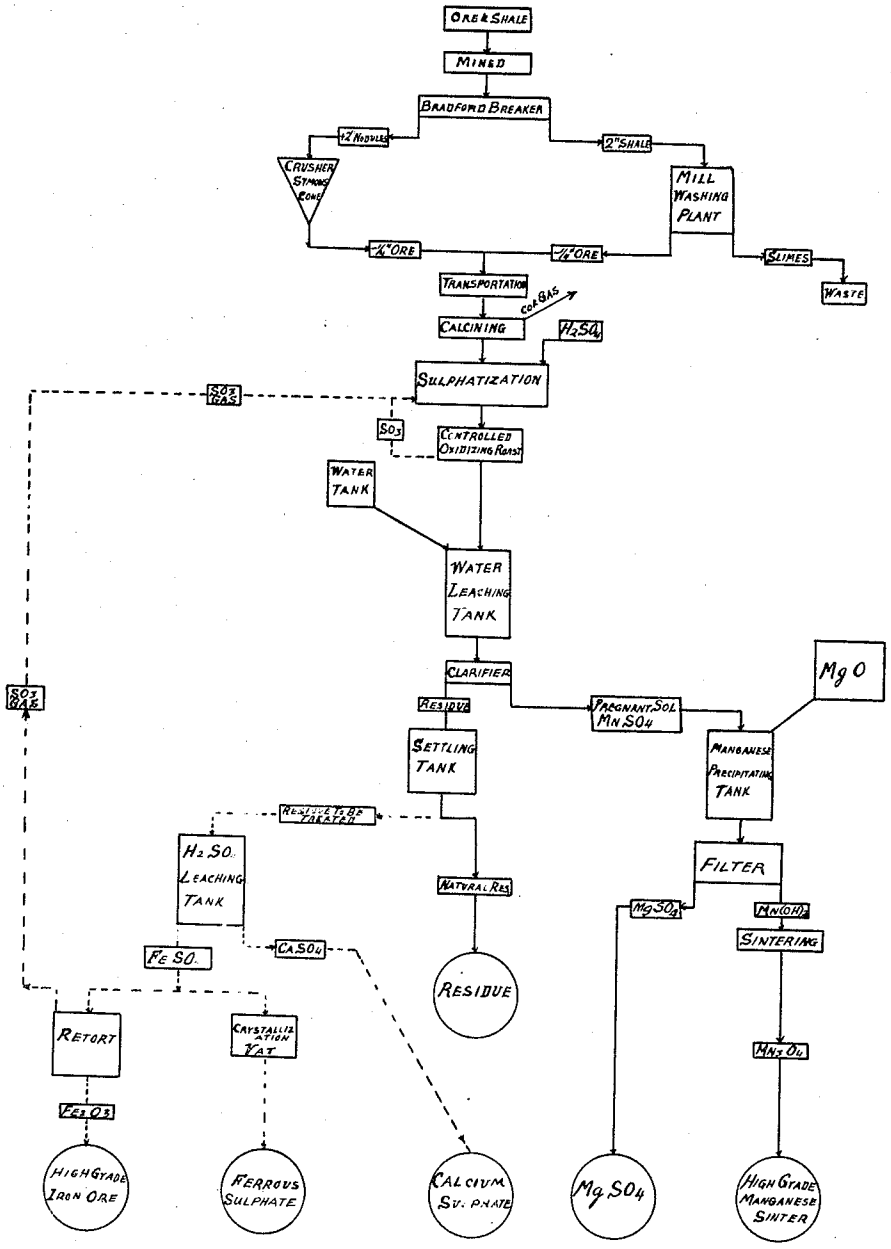
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PROCESS OF EXTRACTING MANGANESE FROM ORE

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PROCESS OF EXTRACTING MANGANESE FROM ORE

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The invention relates to an improved process for separating manganese from its ore, particularly the low grade ores wherein the manganese is associated with relatively large amounts of other materials.

The primary object of the invention is to devise an economical process that can be applied to available manganese deposits and obtain therefrom at a reasonable cost a manganese product in a commercial form.

Another object is to provide a process for obtaining relatively pure manganese oxide free from those impurities which are detrimental in metallurgical processes utilizing the manganese product.

A further object is to provide a process for beneficiating certain manganese bearing materials which heretofore have not been amenable to known methods of treatment.

Other objects are, first, to obtain manganese from complex carbonate ores, mangano-siderites and the like; second, to obtain an efficient method for the separation of manganese from iron in an economical manner; third, to obtain manganese from its ores in a form practically free from phosphorus; fourth, to obtain a chemical process for the separation of manganese from the other materials associated in the ore; and fifth, to obtain a chemical process resulting in by-products of commercial value.

One of the features of our invention is the step of the process in which the separation of the manganese and the iron is effected. This consists in sulphatizing the ore to obtain manganese sulphate and sulphates of other materials associated in the ore and in subsequently subjecting the sulphatized product to a controlled oxidizing roast in which the manganese sulphate remains unchanged and certain of the other sulphates, particularly iron sulphate are oxidized. This renders the mixture in such a condition that when subjected to a water leach the manganese is dissolved and the iron is undissolved and remains as a solid in the oxide form. It has been found that by carefully controlling the temperature at which the sulphatized product is oxidized a very effective separation of the manganese and the iron can be obtained at a low cost.

While in the broader aspects our invention deals with the separation of manganese from other materials such as iron which are ordinarily associated with the manganese in the manganese bearing materials, our invention is particularly applicable to the extraction of manganese from low grade ores such as the complex carbonate ores, mangano-siderites, etc., and in the following detailed description reference will be made to an ore which after being separated from shale assays approximately as follows:

	Per cent
Mn	10 –20
Fe	8 –13
CaO	12 –20
Al_2O_3	1.5 – 2.5
MgO	1.5 – 2.5
SiO_2	13
P	0.4 – 0.7
S	.05

The accompanying drawing discloses a flow sheet for one process of extracting an ore of the above analysis.

The ore and shale as mined is subjected to mechanical action to separate the shale from the ore and as indicated in the accompanying flow sheet it is preferably processed through a Bradford breaker from which the nodules above a certain size, for example two inches, are separated from the remaining material and submitted to a suitable crusher. The fine material is processed through a mill-washing plant from which a certain amount of ore is recovered and mixed with the crushed ore from the crusher. The ore obtained in this manner is then transported to a calcining furnace in which the carbonates are reduced to the oxide form with evolution of carbon dioxide gas. From the calcining furnace the material is obtained in the form of manganese iron and calcium oxides, together with certain other impurities and this material is then subjected to a sulphatizing roast to convert the oxides into manganese iron and calcium sulphates.

The sulphatizing roast may be carried out in various ways, one of which is to add sulphuric acid to the solid material as it is being passed into the roasting furnace. Another method of sulphatizing might be to subject the solid oxide material to the action of sulphur trioxide gas which may be obtained in various ways but preferably through the burning of a sulphur bearing material. It may be found desirable in some instances to add a sulphur ore to the manganese ore and process both together through the sulphatizing furnace. In whatever way the sulphatizing roast is conducted the purpose is to convert the metals into the sulphates, thus forming (with the particular ore above mentioned) managanese sulphate, iron sulphate and calcium sulphate. Following the sulphatizing roast the

material is subjected to an oxidizing roast at a predetermined temperature such that the manganese sulphate will not be decomposed but certain other materials associated with the manganese will be decomposed. Thus with the ore of the analysis given the temperature maintained is between 450° C. and 700° C., the preferred temperature being 650° C. This temperature is high enough to insure complete decomposition of ferric sulphate and is sufficiently under the decomposition point of the manganese sulphate to prevent substantial loss of manganese. The result of the oxidizing roast is to convert the iron into the oxide form while allowing the manganese and the calcium to remain as sulphates. In converting the ferric sulphate into the oxide sulphur trioxide is elvolved which may be introduced into the sulphatizing furnace.

The material resulting from the oxidizing roast is then subjected to a water leach, thereby separating the soluble material from the insoluble. The manganese sulphate is dissolved leaving substantially all of the other materials as a residue, including the iron, calcium and the other impurities in the ore. The phosphorus also remains in the residue at this point, thereby providing an effective separation of the manganese from the phosphorus.

In order to obtain the manganese from the solution it is subjected to a suitable precipitant such as an alkali or an alkaline earth oxide. For example, the solution may be treated with magnesia thereby precipitating manganese hydroxide and leaving magnesium sulphate in solution. The manganese hydroxide is then preferably submitted to a sintering operation in a furnace, thereby converting the same into the oxide Mn_3O_4. The material obtained from the process in this manner is a very high grade manganese sinter substantially free from phosphorus and relatively free from iron, calcium and other impurities.

The by-products from the process as above described are magnesium sulphate or other material resulting from the precipitation and the residue from the leaching tank. This residue contains calcium sulphate, iron oxide and the other impurities found in the ore.

For economical reasons it may be desirable to subject this residue to a further purification and the dotted line portion of the flow sheet shows one method for accomplishing this result. The residue from the leaching operation is submitted to the action of sulphuric acid, thereby converting the iron into soluble ferrous sulphate and leaving the relatively insoluble calcium sulphate. The ferrous sulphate may either be subjected to distillation in a retort for the purpose of obtaining sulphur trioxide gas and iron oxide, or it may be crystallized to obtain a commercial grade of ferrous sulphate. If the distillation method is employed the sulphur trioxide gas may be utilized in the sulphatizing roast as indicated by the dotted line on the flow sheet.

While we have given above one method for extracting manganese from an ore of the analysis heretofore set forth, it is to be understood that the invention in its broader aspects may be embodied in various modified forms. For example, the step of calcining the ore previous to the sulphatizing process may be eliminated in certain instances providing that the direct subjection of the carbonates to the sulphatizing process does not result in too violent an evolution of carbon dioxide gas.

The sulphatizing process may be carried out in various ways, among which are, first, subjecting to a roast in the presence of sulphur compounds; second subjecting to the action of sulphur dioxide or sulphur trioxide gases; and third leaching with sulphuric acid.

When the first and second methods of sulphatization are used the crude carbonate ore is preferably placed directly into the furnace where carbon dioxide gas is evolved, the sulphates formed and the temperature of the furnace is maintained within the ranges previously set forth in order to decompose the soluble iron sulphate into the water-insoluble iron oxide. Where the third method is used, the ore is first treated with sulphuric acid to form a paste before being introduced into the roasting furnace.

The principal feature of our invention resides in the separation of manganese from other metals by sulphatization followed by a controlled oxidizing roast and this phase of the invention may be applied not only to an ore of the analysis given but has a more general application to manganese bearing ores, minerals and metallurgical products. While the process described results in a separation of the manganese from the iron, it is to be understood also that the process has wider application and may be used to separate manganese from other metals capable of forming sulphates whose decomposition temperature is below that of manganese.

In some ores there may also be other metals that will form soluble sulphates whose decomposition temperature is equal to or above that of manganese. These of course will be leached out with the manganese sulphate and must be separated from the manganese by further treatment or else remain in the manganese sinter.

The amount of iron in the solution from the leaching tank can be controlled by varying the time element of the oxidizing roast. If the roasting time is shortened, a larger amount of iron will be found in the manganese sinter. The iron in the final product may also be controlled by variation of the temperature of the roast since a lower temperature will result in less complete conversion of the soluble iron sulphate into the insoluble iron oxide.

From the above description it will be apparent that our process converts a low grade manganese ore having a relatively high percentage of iron and a material amount of phosphorus into a high grade manganese sinter substantially free from phosphorus and containing relatively small amounts of other impurities.

What we claim as our invention is:

1. The method of extracting manganese compounds from complex carbonate ores containing manganese and iron which comprises calcining the ore to eliminate the carbonates, sulphatizing the calcined product, roasting the sulphatized product in the presence of air at a temperature of approximately 650° C. until the iron is oxidized into a condition relatively insoluble in water, leaching with water, separating soluble manganese sulphate from the insoluble residue, precipitating a manganese compound from said solution and heating the precipitate to a tempertaure forming a manganese oxide sinter.

2. The process of extracting manganese from carbonate ores containing the following ingredients: $MnCO_3$, $FeCO_3$, $MgCO_3$, $CaCO_3$, SiO_2, Al_2O_3, which comprises calcining the ore to eliminate the carbonates, sulphatizing the calcined product, roasting the sulphatized product in the presence of air at approximately 650° C. until the iron is

oxidized into a condition relatively insoluble in water, leaching with water, separating soluble manganese sulphate from the insoluble residue, precipitating a manganese compound from said solution and heating the precipitate to a temperature forming a manganese oxide sinter containing manganese as the principal metal.

3. The process of extracting metal compounds from carbonate ores containing the following ingredients: $MnCO_3$, $FeCO_3$, $MgCO_3$, $CaCO_3$, SiO_2, Al_3O_3, which comprises calcining the ore to eliminate the carbonates, sulphatizing the calcined product, roasting the sulphatized product in the presence of air at approximately 650° C. until the iron is oxidized into a condition relatively insoluble in water, leaching with water, separating soluble manganese sulphate from the insoluble residue, precipitating a manganese compound from said solution and heating the precipitate to a temperature forming a manganese oxide sinter containing manganese as the principal metal, treating said insoluble residue from said water leach with sulphuric acid to form soluble iron sulphate, separating the soluble iron sulphate from the insoluble residue and evaporating said iron sulphate solution to crystallize out and recover solid iron sulphate.

4. The process of extracting metal compounds from carbonate ores containing the following ingredients: $MnCO_3$, $FeCO_3$, $MgCO_3$, $CaCO_3$, SiO_2, Al_2O_3, which comprises calcining the ore to eliminate the carbonates, sulphatizing the calcined product, roasting the sulphatized product in the presence of air at approximately 650° C. until the iron is oxidized into a condition relatively insoluble in water, leaching with water, separating soluble manganese sulphate from the insoluble residue, precipitating a manganese compound from said solution and heating the precipitate to a temperature forming a manganese oxide sinter containing manganese as the principal metal, treating said insoluble residue from said water leach with sulphuric acid to form soluble iron sulphate, separating the soluble iron sulphate from the insoluble residue, evaporating and distilling said solution of iron sulphate to obtain insoluble iron oxide resulting in the evolution of sulphur gases and utilizing said gases to sulphatize additional ore.

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