

S. P. KINNEY

METHOD OF RECOVERING MANGANESE

CO-CO₂-H₂

HCL

HCL

STEAM

H₂O

CO-H₂

CO-CO₂-H₂O

FAN

COKE TOWER

H₂O+CO₂ WASTE

HCL

N₂-H₂-CO₂-CO-HCL

H₂-CO

ROTARY OR WEDGE KILN

BURNER

CHARGE

Mn₂O₄

Fe₂O₃

HCL

GANGUE INCLUDING PHOS.

MnCl₂

FeCl₂

CO-CO₂-H₂

CONVEYOR

KILN

HCL

GAS PRODUCER

FE-MN

FE

MAGNETIC SEPARATION

MN INVENTOR.

Selwynne P. Kinney

BY Wilkinson Hensley Byron & Knight

UNITED STATES PATENT OFFICE

2,290,843

METHOD OF RECOVERING MANGANESE

Selwyne P. Kinney, Pittsburgh, Pa., assignor to
Minerals and Metals Corporation, New York,
N. Y., a corporation of Delaware

Application May 26, 1941, Serial No. 395,236

3 Claims. (Cl. 75-21)

This invention relates to a new and improved method of recovering manganese from manganiferous iron ores, and further to such a method adapted for use in connection with low grade iron ores with the subsequent separation of iron.

In the treatment of such ores I have found that in some cases it is more desirable to volatilize the manganese directly out of the ore, or to form a manganese product with a reagent, as, for example, chlorine, and volatilize the manganese chloride from the ore. In the process which is disclosed herein, I have found it is more desirable to take advantage of the phenomena of volatilization and to separate the manganese from the gangue in this manner rather than smelting where a fusion process is employed.

In the manufacture of ferro-manganese and other ferro alloys from manganese ores, a considerable loss is generally encountered due to volatilization of manganese. In the smelting of manganese ores for the production of ferro-manganese in a blast furnace, the ore is mixed with limestone and coke for fuel. The shaft of this furnace is high and comparatively cool and even with a height of shaft of approximately 80 to 100', manganese is volatilized from the charge and the loss in the gases in the form of manganese or partially reduced oxide ranges from a minimum of 8% to sometimes as high as 15%, according to the operation.

I have noticed the tendency of the manganese to volatilize under the above described conditions, and in this invention I make use of volatilization for the recovery of the manganese from its ores and particularly its low grade ores containing large percentages of gangue and iron.

It is an object of the present invention to provide new and improved methods for the recovery of manganese from ores containing this material.

It is a further object to provide processes suitable for use with manganiferous iron ores and from low grade iron ores.

It is also an object to provide a method of this character in which the manganese is volatilized from the ores and is condensed from its volatile form and recovered as metallic manganese and manganese dioxide.

It is an additional object to provide a method by which the manganese may be recovered from the ores in the form of chlorides and the chlorides subsequently treated for the formation of the metallic manganese.

It is another object to provide methods of this character in which iron recovered with the man-

gane may be thereafter separated therefrom, as, for example, by magnetic separation.

Other and further objects will appear as the description proceeds.

I have shown a diagrammatic apparatus layout and flow sheet in the single figure of the accompanying drawing.

In the recovery of manganese from ores, I prefer to mix the ore with carbon and then heat the charge under conditions which are more favorable for volatilization of the manganese. In this operation a hearth of carborundum or other suitable material can be used, which hearth is heated from the bottom and the charge is carried directly upon the hearth. The charge mixed with carbon is raised in temperature to a point where the manganese is volatilized in the form of the oxide and carried out of the roasting furnace with the gases.

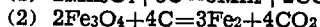
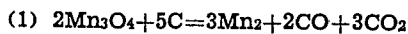
The manganese is then recovered from the gas by using dust collectors of any type, and wet gas washers, or an electric precipitator, or any combination of such means of recovery. The recovered oxide is of a comparatively high purity and may subsequently be reduced in an electric furnace or may be sintered to form a high manganese content product for charging into the blast furnace for the production of ferro-manganese.

In the process of recovery of manganese from low grade ores, the volatilization process may be carried out in any type of retort, coupled with a suitable condensing system for the recovery of the oxide of manganese. The process of volatilization of manganese may also be carried out in a continuous manner on a traveling hearth, for instance, a grated hearth similar to that used in the sintering of ore, or any other hearth capable of withstanding high temperatures. In this case I prefer to mix the charge with carbon and place it on a moving grate or bed. The carbon in the charge is ignited by oil or other suitable means and the mass is raised to a high temperature which permits volatilization of the manganese and manganese oxides. The oxides of manganese and metallic manganese fumes are then recovered from the gas by means of a dust or fume recovery system.

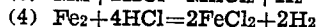
In the recovery of manganese from low grade manganese ores or from low grade manganiferous ores, I have found it possible to effect a separation of manganese and iron or a recovery of manganese alone by the formation of chlorides of these metals. It is a well known fact that chlorides of manganese and iron are easily formed and that these chlorides volatilize at a compara-

tively low temperature. It is also known that the chlorides of these metals may be formed directly from the oxide, although in some cases it is preferable to form them directly from the individual metals.

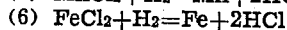
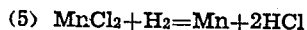
In the process of the recovery of manganese I prefer to make a direct reduction either with gas or solid carbon of the oxides of manganese and iron as a first step. The reactions are as follows:



After reduction, the metals are contacted with hydrochloric acid gas with the resultant formation of manganese and iron chlorides as shown in the following equations covering this second step in the process:



In this second step, I prefer to apply heat to volatilize the manganese and iron chlorides out of gangue material. In the third step, these chlorides are condensed and treated with recirculated hydrogen or hydrogen bearing gas for the formation of metallic manganese and metallic iron and hydrochloric acid gas. The equations are as follows:



In the fourth step, which comprises the separation of the manganese from the iron, I prefer to use a magnetic or other suitable means. By this invention the entire process is carried out at a comparatively low temperature and the metallics in the ore are taken away from the ore by volatilization rather than by melting and fluxing the gangue materials.

In the accompanying drawing, a flow sheet is shown giving a diagrammatic flow of materials through the process. The lower part of the sheet shows diagrammatically the equipment required for reduction, volatilization and condensation and in the upper part of the sheet in diagrammatic form will be found the condensing system for handling the gases used in the process.

The first step in the process consists of charging the ore to a rotary kiln or multiple hearth type furnace in which the charge is dried and reduced with either solid carbon or other suitable means. In this reduction furnace hydro-

chloric acid is brought into contact with the charge and necessary heat is applied to volatilize the manganese and iron chlorides which are condensed in an adjoining chamber. These chlorides are conveyed to a kiln where they are contacted with hydrogen gas, and metallic manganese and iron are formed. The end products from the latter kiln, that is, hydrochloric acid gas and other gases, are conveyed to an ordinary condensing tower where they are contacted with water and thence enter an ordinary condensing system.

The products of combustion from the producer gas which is used in the last kiln are carried along with the hydrochloric gas and passed through the condensing system and any carbon or hydrogen remaining in the system from this combination are recirculated through the last kiln, as shown on the flow sheet.

While I have described in detail certain preferred methods of carrying out my invention, it is capable of modification to meet differing conditions and requirements, and I contemplate such variations as come within the spirit and scope of the appended claims.

What is claimed is:

1. The process for the recovery of manganese from manganese bearing ores, which comprises reducing the ores with carbon, treating the reduced ores with hydrochloric acid, heating and volatilizing the manganese in the form of a chloride, condensing the manganese chloride, and treating the chloride with hydrogen to obtain metallic manganese.

2. The process for the recovery of iron and manganese from ores bearing these metals, which comprises reducing the ores with carbon, treating the reduced ores to form chlorides of iron and manganese, volatilizing and condensing the chlorides, treating them with hydrogen bearing gases to produce metallic iron and manganese, and separating the metals.

3. The process for the recovery of iron and manganese from ores bearing these metals, which comprises treating the ores to reduce iron and manganese oxides, treating the reduced metals to form chlorides of iron and manganese, volatilizing and condensing the chlorides, treating them with hydrogen bearing gases to produce metallic iron and manganese, and separating the metals.

SELWYNE P. KINNEY.