

[54] METHOD FOR PRODUCING MANGANESE
OXIDE PELLETS

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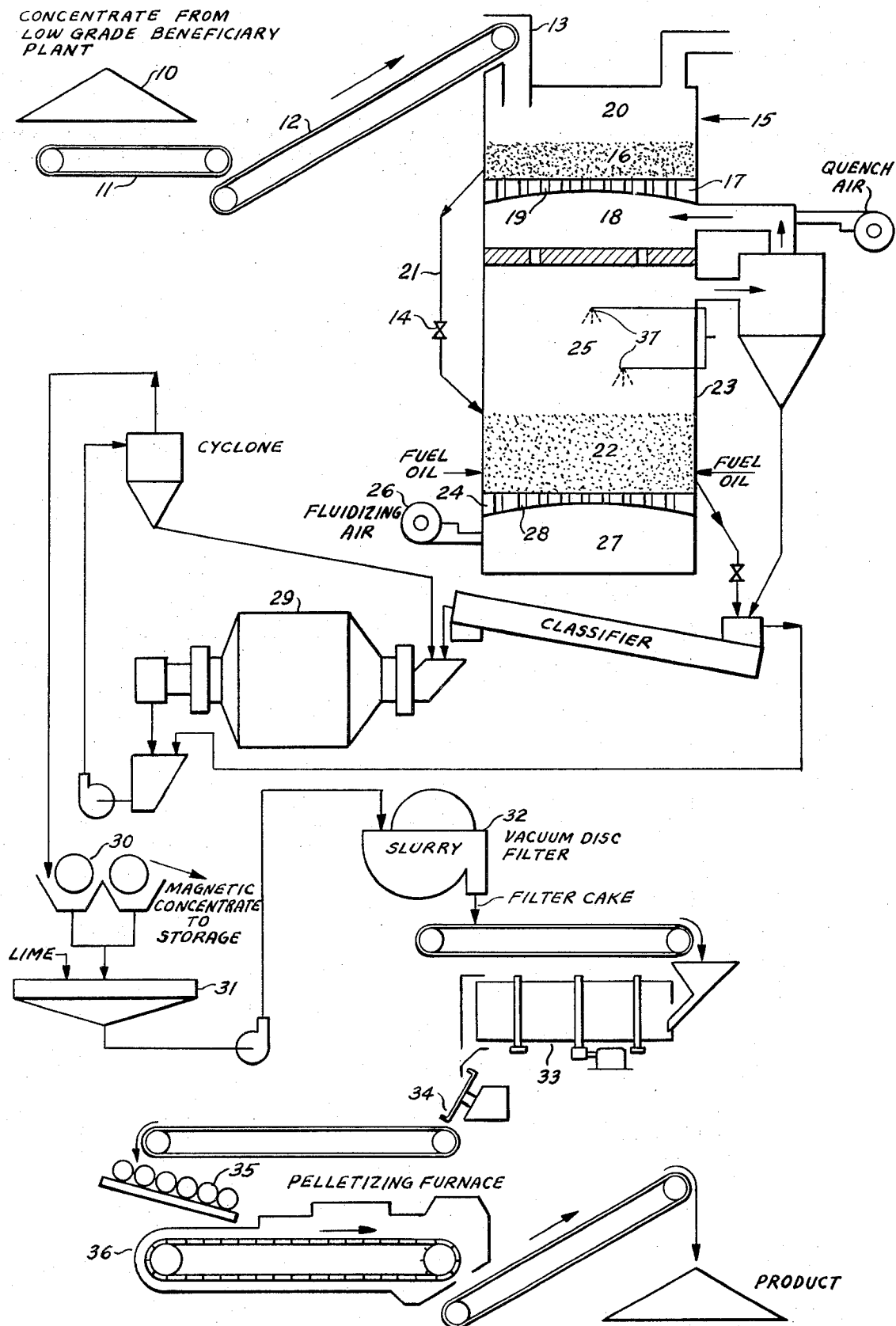
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[57] ABSTRACT

Method for producing manganese oxide pellets from manganese-bearing material such as high grade, medium grade or low grade oxidic or carbonate manganese ores and from waste products which are obtained from high grade and medium grade manganese ore processing plants. The manganese-bearing material is beneficiated to form an upgraded concentrate which includes manganese oxides and non-magnetic iron oxides. The concentrate is roasted to reduce the manganese oxides to mangano-manganic oxide and to reduce a major portion of the non-magnetic iron oxides to magnetic iron oxides. The roasted concentrate is ground and treated magnetically to separate non-magnetic particles from magnetic particles. The ground non-magnetic particles are flocculated, thickened and filtered to thus produce a non-magnetic concentrate which may be partially dried and which is balled and pelletized.

Manganese oxide pellets produced by the method of the invention consist of not less than 48% manganese, not more than 4.0% silica, not more than 7.0% alumina, not more than 1.0% alkali metals, not more than 0.12% arsenic and not more than 6.0% iron, the weight ratio of the manganese to iron in the pellets is between 8:1 to about 20:1.

21 Claims, 1 Drawing Figure



METHOD FOR PRODUCING MANGANESE OXIDE PELLETS

BACKGROUND OF THE INVENTION

This invention is directed to a method for producing manganese oxide pellets from manganese ores. Specifically, the method of the invention is directed to mechanically preparing high grade ore and mechanically and physically preparing medium grade and low grade oxidic and carbonate manganese ores and waste products from high grade and medium grade manganese ore processing plants and pelletizing the concentrate so produced.

Extensive oxidic and carbonate manganese ore deposits in which the primary manganese mineral is pyrolusite (MnO_2), rhodochrosite (MnCO_3), ramsdellite (MnO_2) and alkali-containing manganese minerals such as cryptomelane ($\text{KMn}_8\text{O}_{16}$) are known and mined throughout the world. All the ores contain impurities such as alumina and silica in varying amounts and may contain arsenic. Many of the ore deposits contain more than 45% manganese and are classified as high grade manganese ore deposits. The ore in these deposits is processed by simple mechanical ore preparation operations, such as primary and secondary crushing, screening and washing, to produce a product containing more than 48% manganese, a low incident of impurities and a favorable manganese to iron ratio. The product is commercially attractive and can be used to produce manganese alloys, such as ferro-manganese and the like.

Other ore deposits, which contain between 35% and 45% manganese, are classified as medium grade manganese ore deposits. Because these ores contain a lesser amount of manganese and therefore a greater amount of impurities than do high grade manganese ore deposits, the ores must be beneficiated by more sophisticated physical ore dressing techniques than high grade manganese ores. Nevertheless, the physical ore dressing operations required to increase the manganese content to more than 48% and to reduce the amount of impurities therein and to obtain a favorable manganese grade are relatively inexpensive and the product produced is commercially attractive and can be used to produce manganese alloys such as ferro-manganese and the like.

The ore deposits which contain less than 35% and which can contain as little as 15% manganese are classified as low grade ores. If the iron content is high, the ores are referred to as manganiferous ores. Generally, these low grade ores and waste products for high grade and medium grade manganese ore processing plants are not used in producing manganese alloys, such as ferro-manganese and the like, because of the low manganese content, the high gangue content and an unfavorable or low manganese to iron ratio.

Although known high grade and medium grade ore deposits are fairly extensive and can be processed by relatively inexpensive mechanical and physical ore dressing operations, it is becoming more attractive economically to upgrade or beneficiate low grade ore deposits and the waste products from high grade and medium grade ore processing plants to make them commercially attractive and usable in the production of manganese alloys, such as ferro-alloys and the like. It has been suggested that all manganese ores and in particular low grade ores and waste products from manganese processing plants be beneficiated and formed into

pellets usable as charge material for metallurgical furnaces.

Apparatus and methods of pelletizing iron ores and iron ore concentrates have been known for many years.

Attempts to adapt the same apparatus and methods to upgrade and pelletize manganese ores and manganese ore concentrates have not been notably successful, however. One such method of pelletizing manganese ores is described in U.S. Pat. No. 3,486,880 issued Dec. 30, 1969 to J. Vlatny and titled "Heat Indurated Compacts of Manganese Ore and Process of Making Same." In the described method, manganese oxide ores or concentrates comprised of MnO_2 , Mn_2O_3 and Mn_3O_4 and containing gangue such as silica, alumina, and titania are mixed with fossil fuel and balled. The balled material is fired at about 2300°F. for a time in a reducing or neutral atmosphere, containing little or no oxygen, to reduce the manganese oxide on the surface of the ore particles to MnO and to react the MnO with the acidic impurities, for example, alumina and silica, to form a slag which binds the pellets together. While the above method can be used with high grade manganese ores and concentrates containing small amounts of gangue such as alumina, silica, alkali metals and arsenic, the method cannot be used with ores which contain large quantities of the above impurities since these impurities are not removed in the process. In fact, the formation of a slag in the pellets coats and binds the pellets together at relatively low temperatures such as 2000° F. to 2300° F. making it virtually impossible to reduce the arsenic content of the pellets even at temperatures as low as 2300° F. in a reducing atmosphere within a commercially accepted residence time at temperature. In addition, the presence of large amounts of slag-forming constituents in the pellets requires the addition of large amounts of flux materials, such as calcium carbonate, to the blast furnace during subsequent reduction of the manganese ores to ferro-manganese, thereby increasing the costs of production of the ferro-manganese alloys. Since the amount of alkali metals in the treated manganese material is not reduced, the hazards of early refractory lining failure due to refractory attack during reduction of the treated material in the blast furnace is an ever present danger.

Another method of treating manganese ores is described in U.S. Pat. No. 2,745,730 issued May 15, 1956 to F. O. DeVany. Manganese ores, such as manganiferous iron ores which contain about 8% to 16% manganese and 12% to 35% iron and other low grade deposits, are reduction roasted to produce leachable manganous oxide. The manganese ores are roasted in a shaft-type furnace to convert all the manganese dioxide to manganous oxide and iron oxides to magnetite. All the manganous oxide is leached from the roasted material by an ammoniacal leaching process.

If the manganese ores contain arsenic, it is necessary to remove substantially all the arsenic prior to the use of the manganese ores in the production of manganese and ferro-manganese alloys. Arsenic remaining in the ore is released as a vapor during the smelting of the manganese ores in the blast furnace. This arsenic is deposited in the gas flues of the furnace and is eventually vented to the atmosphere. Therefore, as an environmental control measure, the arsenic in the manganese ores should be removed prior to use in the metallurgical furnaces.

One method used to remove arsenic from iron ores is described in U.S. Pat. No. 2,977,215 issued Mar. 28, 1961 to Kurt Meyer et al. titled "Arsenic Removal and the Pelletizing of the De-Arsenized Material". Meyer uses a neutral atmosphere and a solid carbonaceous reductant and pyrite to reduce the arsenic in balled iron ores. Meyer does not de-arsenize manganese ores. Manganese ores would be reduced to manganous oxide by the use of a solid carbonaceous reductant. In addition, the use of pyrite as disclosed by Meyer et al. will add sulfur to the pellets. Sulfur cannot be tolerated in manganese-bearing materials which are to be subsequently used to produce ferro-manganese and other manganese alloys.

It is the primary object of this invention to provide a method for manufacturing manganese oxide pellets, which method will alleviate the foregoing problems.

It is an additional object of this invention to provide a method for upgrading low grade manganese ores and waste products from high grade and medium grade manganese ore processing plants which are low in manganese and contain relatively large amounts of detrimental impurities and have an unfavorable manganese to iron weight ratio, to produce an upgraded concentrate and to produce manganese oxide pellets from the upgraded concentrate.

It is a further object of this invention to provide a method for producing manganese oxide pellets which contain not less than 48% manganese and are low in detrimental impurities and have a manganese to iron weight ratio greater than 8:1, from high grade manganese ores, medium grade manganese ores, low grade manganese ores and waste products from high grade and medium grade manganese ore processing plants, said pellets being commercially attractive and usable as raw materials to produce manganese alloys such as ferro-manganese and the like.

It is a still further object of this invention to provide a manganese oxide pellet suitable for charging into a blast furnace and electric furnace to produce ferro-manganese alloys and the like.

SUMMARY OF THE INVENTION

Broadly, the method of the invention includes mechanical and gravity beneficiating of oxides and carbonate manganese ores and waste products from manganese ore processing plants to obtain a concentrate which is high in manganese content and subjecting the concentrate to reduction roasting to produce magnetic and non-magnetic particles in the concentrate. The roasted concentrate is treated magnetically to separate the magnetic particles from the non-magnetic particles and to form both a concentrate of non-magnetic particles and a concentrate of magnetic particles. The magnetic concentrate is discarded. The non-magnetic concentrate is then further processed to produce manganese oxide pellets which are commercially attractive and are suitable for use in producing manganese alloys such as ferro-manganese and the like.

DESCRIPTION OF THE DRAWING

The drawing is a schematic diagram of the method of the invention by which oxidic and carbonate manganese ores and waste products from oxidic and carbonate manganese ore processing plants are formed into usable manganese oxide pellets.

DESCRIPTION OF THE PREFERRED EMBODIMENT

We have found that manganese oxide pellets containing not less than 48% manganese, not more than 4.0% silica, not more than 7.0% alumina, not more than 1.0% alkali metals, not more than 0.12% arsenic, not more than 6% iron and having a manganese to iron weight ratio of not less than 8:1, can be made from (a) high grade and medium grade oxidic manganese ores in which the primary manganese mineral is pyrolusite (Mn_2O) or the potassium bearing mineral, cryptomelane ($\text{KMn}_8\text{O}_{16}$) such as Brazilian ICOMI ore, (b) high grade and medium grade carbonate manganese ores in which the primary manganese mineral is rhodochrosite (MnCO_3), (c) low grade manganese ores which can contain pyrolusite or rhodochrosite or psilomelane ($(\text{Ba}_1\text{H}_2\text{O})_2\text{Mn}_5\text{O}_{10}$), and (d) waste products from high grade and medium grade oxidic and carbonate manganese ore processing plants. The oxidic and carbonate manganese ores and waste products, which can be pelletized by the method of the invention, have a chemical composition within the broad ranges shown below in Table I:

TABLE I

Ranges of Chemical Compositions of Manganese-Ores and Waste Products	
Constituent	% Constituent
Manganese	15-50
Iron	5-15
Alumina	4-15
Silica	2-12
Sodium	0.10-0.50
Potassium	0.5-2.5
Arsenic	0.20-0.30
Water of Hydration	3-15
Manganese/Iron Ratio	1/1-10/1

Hereinafter when constituents of oxidic and carbonate manganese ores and waste products from oxidic and carbonate manganese ore processing plants are mentioned in the specification and claims they are reported as follows:

Manganese is calculated as elemental manganese, iron is calculated as elemental iron, sodium and potassium are calculated as oxides (Na_2O and K_2O , respectively), silica is calculated as SiO_2 and alumina is calculated as Al_2O_3 and arsenic as elemental arsenic. The percentages of the constituents reported in these specifications and claims are on a weight basis unless otherwise noted.

As noted previously, high grade and medium grade oxidic and carbonate ores are processed by relatively simple mechanical operations. The raw ore is crushed, screened and washed to produce a commercially acceptable coarse product having a particle size of $-2, +\frac{1}{2}$ inch. The coarse upgraded product has a chemical composition within the ranges shown below in Table II:

TABLE II

Chemical Compositions of Coarse Product From High Grade and Medium Grade Manganese Ore Processing Plants	
Constituent	% In Product
Manganese	48-56
Iron	4-6
Silica	1.5-4.5
Alumina	4.5-6.5
Sodium	.15-.25
Potassium	1.0-2.3
Phosphorus	About .1
Arsenic	.10-.25
Water of Hydration	3-5
Manganese/Iron Ratio	8/1-14/1

Because the coarse particles have a manganese content above 48%, are low in residual impurities, such as silica and alumina, and have a manganese to iron weight ratio of more than 8:1, they can be shipped as a usable product.

In the mechanical operations noted above, two other sizes of particles are produced, namely, a medium size, $-\frac{1}{2}$ inch, +20 mesh (U.S. Series Sieve) and a fine size, -20 inch, +100 mesh (U.S. Series Sieve). The medium and fine size particles are low in manganese content, high in iron and other impurities and have an undesirable manganese to iron ratio as shown below in Table III, which shows a typical range of chemical compositions:

TABLE III

Typical Chemical Composition of Medium and Fine Size Particles from Manganese Ore Processing Plants		
Constituent	% in Product	
	Medium Size Particles	Fine Size Particles
Manganese	36-46	28-40
Iron	7-14	9-15
Silica	3-6	9-14
Alumina	7-10	10-13
Sodium	.15-.20	.07-.11
Potassium	1.30-1.45	.85-1.0
Phosphorus	About .1	About .1
Arsenic	.17-.25	.20-.26
Water of Hydration	5-12	6-15
Manganese/Iron Ratio	3/1-6/1	1/1-3/1

Because the medium and fine particles are of an undesirable size and low in manganese content, high in iron content and other impurities and have a low manganese to iron weight ratio, the particles are not commercially saleable and are either passed to waste or are stored.

We have found that the medium and fine size particles mentioned above can be beneficiated and processed into a manganese oxide concentrate which can be processed into manganese oxide pellets containing a high manganese content, low iron and other impurities content and a desirable manganese to iron weight ration of not less than 8:1. The pellets can be used to produce manganese alloys such as ferromanganese alloys and the like. A gravity-type separation to reduce the amount of silica and alumina in the particles is made in gravity-type separators, for example, heavy media dynawhirlpools can be used for medium size particles and Humphrey's Spirals for fine size particles. Since sodium is usually associated with silica and alumina in complex silicate compounds, the sodium con-

tent in the particles is removed with the silica and alumina. The upgraded medium and fine particles are mixed together to form a concentrate which can have a typical chemical composition as shown in Table IV below:

TABLE IV

Typical Chemical Composition of a Mix of Medium Size Particles and Fine Size Particles after Upgrading in Gravity-type Separators	
Constituent	% Constituent
Manganese	45-52
Iron	7-14
Silica	1.0-4.0
Alumina	3.0-6.0
Sodium	0.1-0.2
Potassium	0.6-2.0
Phosphorus	About .1
Arsenic	.18-.25
Water of Hydration	3-6
Manganese/Iron Ratio	3/1-7/1

From the above typical chemical composition, it can be seen that the manganese to iron weight ratio is less than 8 to 1 and that the iron content, the alkali metal content, specifically potassium, and the arsenic content are high, therefore the concentrate is undesirable for use in metallurgical furnaces. We have found that the manganese concentrate of medium and fine size particles can be beneficiated, that is, the manganese content increased, the iron content and potassium content decreased and the water of hydration eliminated by treating the concentrate in a two-step reduction roasting process. In the two-step reduction roasting process a substantial portion of the iron, which is present as non-magnetic iron oxide (Fe_2O_3), is reduced to magnetic iron oxide (Fe_3O_4). The magnetic iron oxide (Fe_3O_4) can be separated from the non-magnetic particles such as manganese oxide particles and iron oxide (Fe_2O_3) particles in the roasted concentrate by magnetic means, such as magnetic separators, to thereby reduce the amount of iron and increase the amount of manganese in the concentrate to thereby obtain a favorable manganese to iron weight ratio. Coincidentally with the reduction of non-magnetic iron oxide (Fe_2O_3) to magnetic iron oxide (Fe_3O_4), the manganese compounds in the concentrate, such as manganese dioxide (MnO_2) and cryptomelane ($\text{KMn}_8\text{O}_{16}$) are first reduced to manganic oxide (Mn_2O_3) and then to the tetragonal crystal-line form of hausmannite which is mangano-manganic oxide (Mn_3O_4). Of course, a minor portion of the mangano-manganic oxide (Mn_3O_4) is reduced to manganous oxide (MnO). The non-magnetic concentrate can be processed in subsequent steps to produce manganese oxide pellets which can be used to produce manganese alloys.

The manganese concentrate, that is, the mixture of medium and fine particles which have been treated in the gravity-type separators, is reduction roasted in a two-step process in a fluid solids reactor. The manganese concentrate is dried in an upper compartment of the fluid solids reactor and is passed to a lower compartment wherein a reducing atmosphere generated by the incomplete combustion of fuel oil is provided to obtain the desired results.

Turning now to the attached FIGURE, the concentrate 10 from the dynawhirlpools (not shown) and Humphrey's Spirals (not shown) is fed to a fluid solids reactor 14 by means of a conveyor system 11 and 12

and a chute 13 above the fluid solids reactor 14. The concentrate 10 drops from the conveyor 12 into the chute 13 which feeds the concentrate 10 into an upper or preheating compartment 15 of the fluid solids reactor 14. The particles of the concentrate 10 are dried, dispersed and form a fluid bed 16 on the upper dome 17 by hot combustion gases flowing upwardly through the fluid bed from the hot wind box 18. The hot combustion gases which are at a temperature of about 1022° F. to about 1500° F. (500° C to 815° C) flow from the hot windbox 18 upwardly through a plurality of slots 19 in the upper dome 17 and heat the fluid bed 16. A space or free board 20 is provided above the fluid bed 16 in the upper compartment 15. The concentrate is heated to a temperature of about 302° F. to about 392° F. (150° C-200° C). The two-step roasting process is continuous, that is, concentrate 10 is continuously fed onto the top of the fluid bed 16 in the upper compartment 15 of the fluid solids reactor 14 and a steam of preheated concentrate is continuously drawn out of the upper compartment 15 from the bottom of the fluid bed 16 and is fed to a second fluid bed 22 in the lower compartment 23 of the fluid solids reactor 14 by means of conduit 21. The free moisture in the concentrate, which can be about 5% to about 15% based on the weight of the concentrate, is driven off and the preheated concentrate which is drawn off from the upper compartment at a temperature of about 392° F. (200° C) is bone dry. A portion of the water of hydration, about one tenth thereof, is also removed from the concentrate in the upper compartment 15. The dried concentrate is transferred from the upper compartment 15 to the lower compartment 23 of the fluid solids reactor 14 and is discharged onto the lower dome 24 in the lower compartment 23 to form a relatively deep fluid bed 22. A large free board 25 is provided in the lower compartment 23 above the fluid bed 22. An air blower 26 supplies fluidizing air at a temperature of about 158° F. to 194° F. (70° C to 90° C) to a cold wind box 27 from which the air is blown upwardly through the fluid bed 22 by means of a plurality of slots 28 in the lower dome 24. Fuel oil, for example, No. 6 oil, is incompletely burned at the bottom of the fluid bed 22 in the lower compartment 23. The concentrate is preferably heated to a temperature range of about 1292° F. to 1391° F. (700° C to 755° C) and more preferably within the upper half of the temperature range, in the lower compartment 23. The combustion of the fuel oil and air at the bottom of the fluid bed 22 in the lower compartment 23 forms an atmosphere rich in carbon monoxide (CO) and hydrogen (H₂). In this environment the manganese dioxide (MnO₂) or the cryptomelane (KMn₈O₁₆) is thermally decomposed in several stages and reduced. The first decomposition of the cryptomelane (KMn₈O₁₆) is to manganic oxide (Mn₂O₃) and the second decomposition is to the tetragonal crystalline form of hausmannite, which is manganomanganic oxide (Mn₃O₄). A major portion of the non-magnetic iron oxide (Fe₂O₃) is reduced to magnetic iron oxide (Fe₃O₄). A minor portion of the manganomanganic oxide (Mn₃O₄) is reduced to manganous oxide (MnO). Because at elevated temperatures, for example, 1598° F. to 1800° F. (870° C to 990° C) and above, the fine particles in the concentrate become softer and tend to stick to each other and to refractory and metal surfaces, cooling water 37 is sprayed into the free board 25 above the fluid bed 22 and into the fluid bed 22 it-

self in the lower compartment 23 to keep the temperature of the fluid bed 22 below about 1598° F. (870° C) and of the exit gases leaving the free board 25 below about 1472° F. (800° C). As noted above, the concentrate is preferably roasted at a temperature within the range of about 1292° F. to 1391° F. (700° C to 755° C), however, the roasting process in the lower compartment 23 is operative within a temperature range of about 1112° F. to 1598° F. (600° C to 870° C). The fluidizing and combustion air is passed upwardly into the fluid bed 22 through slots 28 in the lower dome 24 of the cold wind box 27. The amount of air passed upwardly through the slots 28 is sufficient so that the air space velocity is high enough to fluidize the coarser particles of concentrate. It has been found that the exit gases in the atmosphere in the free board 25 above the fluid bed 22 in the lower compartment 23 of the reactor 14 should contain a high percentage of carbon dioxide and a low percentage of oxygen to obtain the most beneficial results of the invention. The exit gases from the roasting step should contain about 28% to about 30% carbon dioxide, about 0.5% to about 1% oxygen, about 0.5% to about 1% hydrogen and carbon monoxide and about 0.5% to about 1% methane. We have found that the amount of oxygen present in the exit gases in the free board 25 which are cycled into the upper drying portion of the fluid solids reactor 14 is indicative of the manganese to iron ratio which can be expected in the concentrate after magnetic separation. The amount of oxygen in the exit gases is controlled by the amount of fuel which is burned in the fluid bed 22 in the lower compartment 23 of the reactor 14. The manganese to iron ratio in the manganese concentrate after magnetic separation varies inversely with the amount of oxygen in the exit gases in the free board 25, that is, high oxygen contents indicate low manganese to iron ratios, for example, 3:1, and low oxygen content favors high manganese to iron ratios, for example 8:1 or more. Oxygen contents in the exit gases of about 5% result in a manganese to iron ratio of about 5:1 whereas oxygen contents of 3.0% and 1.0% or less result in a manganese to iron ratio of about 12:1 and 15:1 or higher, respectively. Since the amount of oxygen in the exit gases in the free board 25 is critical, we burn an amount of fuel in the lower compartment 23 sufficient to obtain an oxygen content of not more than 4% and preferably not more than 1.0% in the free board 25 of the lower compartment 23. Of course, it is possible to burn sufficient fuel oil to obtain a zero percent of oxygen in the exit gases in the free board 25 of the lower compartment 23. However, carbon monoxide, hydrogen and methane (CO, H₂ and CH₄) are also present in the free board 25, therefore the higher limit of the oxygen content is critical. We prefer to use a No. 6 fuel oil. A typical analysis of No. 6 fuel oil is shown below:

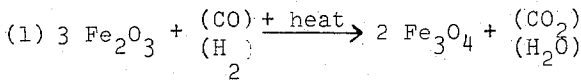
C - 85.4

H₂ - 11.0

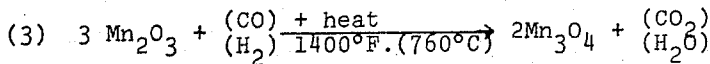
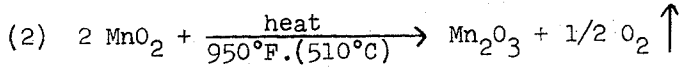
S - 3.2

and incidental residuals, such as water, and has a density of 0.976 grams per cubic centimeter at 60° F, and a gross calorific value of 18,510 BTU per pound.

The iron oxide (Fe₂O₃) present in the concentrate as non-magnetic iron oxide is reduced to ferrous-ferric iron oxide [(Fe₃O₄) which alternatively can be written (FeO.Fe₂O₃)], which is a magnetic iron oxide, in the lower compartment 23, according to the following reaction:

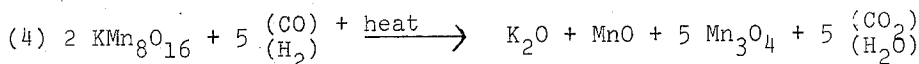


The manganese dioxide (MnO_2) is also reduced in the lower compartment 23 of the reactor 14 according to the following reactions:



of course, a minor portion of the manganomanganic oxide (Mn_3O_4) is reduced to manganous oxide (MnO). The reduction of manganomanganic oxide (Mn_3O_4) to manganous oxide (MnO) is kept to a minimum because the manganous oxide (MnO) consumes unnecessary large amounts of the reductant gases (CO and H_2) thereby requiring higher fuel consumption. Reaction (3) above is accomplished at relatively low temperatures such as $1400^\circ\text{F. (760}^\circ\text{C)}$ by the use of a reducing atmosphere containing carbon monoxide (CO) and hydrogen (H_2) rather than high temperature reduction such as $1724^\circ\text{F. (940}^\circ\text{C)}$ because the fine particles of the concentrate begin to fuse together and sinter at temperatures of about $1472^\circ\text{F. (800}^\circ\text{C)}$. If the particles in the concentrate fuse together and sinter, the operation of the fluid bed is physically upset because the flow of gases upwardly through the bed is effectively stopped, hence reduction of either iron oxide or manganese oxide cannot take place. Of course, if sinter is formed it must also be broken up before it can be removed from the fluid solids reactor.

In manganese ores, of example, Brazilian ores such as ICOMI ore, which contain the mineral cryptomelane ($\text{KMn}_8\text{O}_{16}$) as the major manganese constituent, the potassium in the mineral cannot be removed by ordinary means such as washing since the mineral is insoluble in water. The potassium atom is trapped and randomly distributed in the crystal lattice of the cryptomelane to maintain ionic balance and cannot be expelled from the crystal lattice. Unexpectedly, it has been found that the complex chemical compound, $\text{KMn}_8\text{O}_{16}$, is broken down in the two-step reduction roasting to water soluble potassium oxide (K_2O), a minor portion of manganous oxide (MnO) and a substantial portion of manganomanganic oxide (Mn_3O_4) according to the following reaction:



A major portion of the water soluble potassium oxide (K_2O) is removed in subsequent physical dressing steps involving slurring with water. The removal of (a) the oxygen from the oxides, and (b) of water of hydration during roasting and (c) of potassium during slurring results in a concentrate which pelletizes, that is, can be balled and heated to elevated temperatures to harden the balls and form pellets therefrom, without danger of the explosive release of water of hydration during early drying steps and oxygen during the preheating and hardening steps and without the danger of fusion of the pellets during elevated heating for arsenic removal. The explosive release of water of hydration has resulted in the failure of several previous attempts to produce

manganese oxide pellets since the water of hydration is released at a time during which the green balls are weakest, resulting in the shattering of the balled material. Pelletizing manganese dioxide (MnO_2) at elevated temperatures causes oxygen to be released during the thermic decomposition of the manganese dioxide

(MnO_2) to manganomanganic oxide (Mn_3O_4). The release of oxygen also results in shattering or badly cracking the balled material. Therefore, reducing the manganese dioxide (MnO_2) to manganomanganic oxide (Mn_3O_4) in the reduction roasting step decreases the possibility of oxygen release during pelletizing. Because gangue, such as alumina and silica, forms liquids at low temperatures, the removal of a substantial portion of the gangue prevents the fusion of the pellets during the final high temperature heating stage to remove arsenic. If fusion should occur, arsenic removal is made more difficult, if not impossible. Because the alkali metals, potassium and sodium, attack the refractory lining in a blast furnace, the removal of a major portion of the sodium and potassium decreases the danger of refractory attack when pellets of the invention are treated in the blast furnace. Sodium is usually associated with the alumina and silica and hence is removed with gangue during washing and gravity concentration steps. Arsenic can be present in pyrolusite (MnO_2) and cryptomelane ($\text{KMn}_8\text{O}_{16}$). When the manganese ores are reduction roasted a low order tetragonal form of hausmannite (manganomanganic oxide Mn_3O_4) is formed. The arsenic is present in the crystal lattice of the low order tetragonal form hausmannite. Upon heating the low order tetragonal form of hausmannite to $2250^\circ\text{F. (1205}^\circ\text{C)}$ in a neutral or slightly reducing atmosphere or to $2650^\circ\text{F. (1454}^\circ\text{C)}$ in an oxidizing atmosphere, a thermic allotropic change to a well defined cubic form occurs in the hausmannite. During the thermic allotropic change, arsenic is rejected from the hausmannite crystal. However, it is not possible to reject more than about 75% of the arsenic from the hausmannite under commercial operating conditions. Arsenic is a tramp element in both iron and steel and therefore its removal or reduction to a minimum is essential.

Returning now to the FIGURE, because particles of the concentrate can contain both iron oxides and manganese oxides, the roasted particles are broken down or reduced in size in a grinding mill 29, for example, a ball mill and the like, wherein the particles are reduced to liberation size to separate or liberate the manganese oxides from the iron oxides. It has been found that the liberation size, commercially speaking, is about -100 mesh. It has also been found that -100 mesh is a size suitable for balling the concentrate.

After grinding, the concentrate is passed to magnetic separators 30 where substantially all the magnetic iron oxide (Fe_3O_4) particles are separated from the non-magnetic iron oxide (Fe_2O_3) and manganese oxide par-

ticles to form a magnetic concentrate and a non-magnetic concentrate. The magnetic iron oxide (Fe_3O_4) concentrate is passed to storage for future use as a source of iron or can be discarded as waste material. Since the magnetic concentrate has a high iron oxide content it can be beneficiated and processed into iron oxide or metallic iron pellets and it is therefore preferred to store the concentrate. Of course, the magnetic iron oxide (Fe_3O_4) concentrate will usually contain some residual manganese oxides. This, however, is an advantage in the future use of this waste material as a source of iron to produce steel. The non-magnetic manganese concentrate is flocculated with lime to improve the settling characteristics of the particles in the non-magnetic concentrate. It has also been found that lime introduced to flocculate the non magnetic manganese concentrate combines with the manganese oxides during pelletizing to form a refractory calcium manganate. Pellets produced from manganese non-magnetic concentrate which have more than about 1.5% lime (based on 100 pounds of concentrate), added to the concentrate, contain more hausmannite in the cubic form than do pellets made from a concentrate containing less than 1.5% lime added thereto. A dense shell of manganous oxide forms on pellets made from a concentrate with low lime additions. It is, therefore, preferred to add about 1.5% lime to the non-magnetic manganese concentrate during the flocculating step. The flocculated non-magnetic manganese concentrate is thickened in a thickener 31 and filtered in filter 32 to produce a filter cake. The filter cake is partially dried in drier 33 and is passed to a balling apparatus 34, such as a balling cone, disc, drum, flying saucer or the like. No binders are generally required to ball the non-magnetic manganese concentrate, however, binders such as bentonite can be used to ball the non-magnetic manganese concentrate if desired. If the non-magnetic manganese concentrate contains more than about 16% moisture, it is dried prior to balling. Drying is not required if the non-magnetic manganese concentrate contains about 8% to 14% moisture. If the non-magnetic manganese concentrate contains less than 8% moisture, sufficient moisture to obtain about 8% to 14% moisture, based on the surface area of the particles in the non-magnetic manganese concentrate, is added to the non-magnetic manganese concentrate before balling. The non-magnetic manganese concentrate is formed into balls varying in size from one-fourth inch in diameter to three-fourths inch in diameter.

The balled non-magnetic manganese concentrate is fed onto a roller screen feeder 35 to remove the minus one-fourth inch fraction of fines and to feed the + $\frac{1}{4}$ inch balls into a pelletizing furnace 36, such as a multi-zoned travelling grate furnace or the like.

The balls are initially dried in the pelletizing grate at an air temperature of about 500° F. to about 800° F. to remove free moisture from the balls. If the balls are charged into a multi-zoned travelling grate furnace the drying can occur in the first or first and second zones of the furnace.

The balls should be dried at a rate sufficiently slow to prevent disintegration of the balls by vaporized moisture driven off in the drying stage. In a travelling grate furnace the time can vary from as little as three minutes to as much as ten minutes dependent upon the amount of moisture to be removed and the temperature of the hot gases which are passed through the bed of moist balls.

The balls are then preheated to a temperature of

about 1650° F. to about 1800° F. for a time, for example, about 5 minutes, by hot combustion gases passing downwardly through the balls. In a multi-zoned travelling grate furnace this stage would occur in the third zone of the furnace.

After preheating, the balls are heated by hot combustion gases passing downwardly through the bed of balls to heat them to a temperature range of about 2200° F. to 2650° F. wherein the balls will be hardened to form pellets and a major portion of the arsenic removed from the pellets. In this stage of pelletizing in a multi-zoned travelling grate furnace, the pelletizing stage is divided into a first portion occurring in the fourth zone of the furnace and a second portion occurring in the fifth zone of the furnace. In the first portion of the fourth zone the balls are heated to between about 2200° F. to about 2450° F. for a time, for example, 20 minutes, and are hardened to form pellets. Little arsenic is removed in the first portion of the fourth zone so that the waste hot combustion gases from this portion are recycled in the system and are used in the drying and preheating zones of the furnace. In the second portion of the fourth zone of the furnace the pellets are heated to between about 2450° F. and 2650° F. (1342° C to 1454° C) for a time, for example, about 5 minutes. Additional hardening of the pellets occurs and a major portion of the arsenic in the pellets is volatilized and removed from the furnace in the waste hot combustion gases. Because the waste hot combustion gases contain arsenic, the gases are exhausted either to the atmosphere or to a suitable pollution control apparatus.

The pellets are then cooled by cooling air which is passed upwardly through the pellet bed for a time to reduce the temperature of the pellets to about 150° F., at which temperature the pellets are discharged from the furnace. In a multi-zoned travelling grate furnace the cooling stage will occur in a fifth zone of the furnace and will occur in two stages. In the first stage the pellets will be cooled to about 1800° F. which can take, for example, about 10 minutes. The cooling air contains arsenic and is therefore passed to waste with the waste hot combustion gases from the arsenic removal stage. The pellets are further cooled to about 150° F. in a second cooling stage. Gases from this stage can be recycled and reheated to be reused in the drying, preheating and pelletizing steps.

Pellets treated according to the method of the invention have a typical chemical composition as shown in Table V as follows:

TABLE V

Chemical Composition of Pellets Made by the Invention		
Constituent	% Constituent	
Manganese	58-60	
Iron	5-3	
Silica	2-4	
Alumina	5.5-6.0	
Sodium	0.1-0.15	
Potassium	0.5-1.0	
Phosphorus	0.08-0.10	
Arsenic	0.03-0.10	
Manganese/Iron Ratio	10/1-20/1	

While the above typical chemical composition shows a manganese to iron ratio of 10:1 or higher, pellets having a ratio of 8:1 can be made by the invention and are usable product; however, it is preferred to have a manganese to iron ratio of between 10:1 to 20:1.

As previously noted, a major portion of the alumina and silica is removed in the gravity-type separations prior to roasting. Of course, if coarse particles of high

grade and medium grade manganese ores are being treated, the gravity-type separation can be dispensed with prior to roasting because the alumina and silica contents are below the desired amounts. The ores are roasted and treated as previously described to produce mangano-manganic oxide pellets. Heating the balled concentrate to temperatures as high as 2650° F. does not result in producing a significant amount of liquid slag in the pellets. When the pellets are heated in the range of about 2550° F. to about 2650° F. no fusion difficulty is observed and a major portion of the arsenic in the pellets is removed. The arsenic content of the pellets is effectively decreased to below an acceptable amount, for example, about 0.1%. Arsenic is present as a metallic inclusion in the crystal lattice of the manganese oxide and at temperatures of 2550° F. to 2650° F. is expelled from the lattice as a vapor.

During roasting the manganese dioxide (MnO_2) is reduced to mangano-manganic oxide (Mn_3O_4) with a loss in weight of about 13%. The mangano-manganic oxide (Mn_3O_4) concentrate is soft, porous and poorly crystalline. The balls formed from this material are porous and weak. We, therefore, use a travelling-type grate furnace rather than a dual process grate-kiln furnace to pelletize the balls of mangano-manganic oxide (Mn_3O_4). We have found that pelletizing balls of mangano-manganic oxide (Mn_3O_4) at temperatures of about 2200° F./2250° F. produced relatively weak pellets having a tumble index (% plus one-fourth inch) of 80% to 83% and a porosity of 20%. The pellets are not strong enough to resist degradation during transport. However, balls of mangano-manganic oxide (Mn_3O_4) pelletized at higher temperatures of about 2300° F. to 2400° F. produced pellets which begin to shrink, the particles coalesce and a less porous-more dense, well-bonded structure is formed. Heating the balls to higher temperatures up to 2650° F., the temperature at which arsenic is vaporized, causes the pellets to shrink still further, increases coalescence, decreases porosity to between 5% and 15% and increases the strength of the pellets. Balled mangano-manganic oxide (Mn_3O_4) fired at 2550° F./2650° F. formed pellets having a tumble index (%) of between 90% to 95%. The tumble index (%) is an indication of the strength of the pellets. Commercially acceptable pellets should have a tumble index of more than 90% as determined by ASTM E-69 tumble test in which an amount of pellets, 2 pounds or 25 pounds, is charged into a drum which is 3 feet in diameter and 18 inches long. The drum is rotated at 24 revolutions per minute for 200 revolutions. The material charged into the drum is screened on a ¼ inch screen. The percent of pellets which are one-fourth inch or larger in diameter is taken as the tumble index (%).

While we have described the invention in connection with the treatment and upgrading and pelletization of waste products from high grade manganese ore processing plants, it will be understood that the method of the invention is also applicable to pelletizing all upgraded oxidic and carbonate high grade and medium grade manganese ores having a manganese content of about 35 to 50% manganese, about 10% to 15% iron, not more than 8% silica, not more than 10% alumina, up to 2.2% alkali metals, from 8.18 to 0.25% arsenic, about 3 to 8% water of hydration and, a manganese to iron weight ratio of not more than about 7:1, without subjecting the upgraded concentrate to gravity-type

separation. Of course, all the concentrates produced from the above ores must be roasted to accomplish the results of the method of the invention, that is, a major portion of the non-magnetic iron oxide is converted to magnetic iron oxide which can be separated by magnetic means from the non-magnetic manganese oxides. Of course, manganese ores which contain cryptomelane ($\text{KMn}_8\text{O}_{16}$) will also benefit from the roasting step since the insoluble potassium manganese oxide ($\text{KMn}_8\text{O}_{16}$) is decomposed into the water soluble potassium oxide (K_2O) and mangano-manganic oxide (Mn_3O_4). Water of hydration will be removed as well as oxygen. Arsenic will be removed from pellets made from these ores when heated to temperatures of about 2550° F. to about 2650° F. without the formation of appreciable amounts of liquid slag. Likewise the roasting of the manganese ores prior to balling and pelletizing of the balls by high temperature treatment converts the manganese from a higher to a lower oxidation state so that an explosive release of oxygen from the oxidized manganese minerals such as MnO_2 during high temperature treatment of the balled manganese material will not cause shattering or cracking of said balls.

Processing low grade manganese ores, that is, those ores containing less than about 35% manganese, by the method of the invention requires grinding the ores to a liberation size and separation of the particles in gravity-type separators to upgrade the material prior to roasting.

In a specific example of the invention, 70 tons of medium size particles, ¾ inch × +20 mesh, (U.S. Series Sieve) and 30 tons of fine size particles, -20 mesh × 100 mesh, (U.S. Series Sieve) were processed in mineral jigs and Humphrey's Spirals respectively. The chemical composition of the medium size particles and fine size particles before and after treatment is shown in the following table:

Component	% Component			
	Medium Size Particles		Fine Size Particles	
	Before	After	Before	After
Manganese	41.6	47.7	34.6	47.1
Iron	8.7	6.8	11.4	8.0
Silica	4.5	2.5	10.8	4.2
Alumina	8.5	5.5	11.2	4.8
Sodium (Na_2O)	0.17	0.18	0.09	0.11
Potassium (K_2O)	1.37	1.58	0.92	1.03
Phosphorus	0.10	0.10	0.10	0.10
Arsenic	0.21	0.21	0.23	0.24

The medium size particles and fine size particles were mixed to form one composite batch. The batch was dried and then fed continuously into a fluid-bed type roaster. The particles were roasted at about 1500° F. in a reducing atmosphere containing CO and H_2 . The average retention time was about 20 minutes. The particles were then ground in a ball mill to about 64% minus 325 mesh and about 95% minus 65 mesh and passed to a magnetic separator for wet separation into magnetic particles and non-magnetic particles. About 14% of the particles based on the weight fed to the magnetic separators were separated as magnetic particles and were passed to storage. The remaining 86% of the particles, classed as non-magnetic, were flocculated with lime, the addition being about 2.0% lime based on the weight of the non-magnetic concentrate. The flocculated non-magnetic concentrate was filtered, partially dried and

fed to a disc-type balling apparatus for balling. The particles were formed into balls which average about five-eighths inch in diameter in size and were charged into a pot-grate furnace in batches of about 60 pounds. The balls were heated to a temperature of about 750° F. by hot gases passing upwardly through the balls. After being dried for about 7 minutes, the balls are dried in a second drying step wherein hot gases were passed downwardly through the balls to raise their temperature to about 650° F. for about 3 minutes. The dried balls were then preheated in a third or preheating step. The temperature of the balls was raised to about 1800° F. in about 2 minutes by hot gases passing downwardly through the balls.

The balls were heated in a fourth or heat hardening step. The temperature of the balls was raised to about 2650° F. for about 17 minutes by hot gases passing downwardly through the balls, at which temperature a major portion but not all of the arsenic was removed from the pellets. The balls have now been hardened into pellets.

The pellets were cooled in a fifth step to about 1800° F. by cooling gases passing downwardly through the pellets.

The pellets were cooled by cooling air passing upwardly through the pellets in a sixth step. The temperature of the pellets was lowered to between 150° F. and 200° F. The pellets were discharged from the furnace. A chemical analysis of a sample of the pellets showed the pellets to have the following chemical composition:

Component	% Component
Manganese	59.2
Iron	4.8
Silica	3.1
Alumina	5.3
Sodium (Na ₂ O)	0.15
Potassium (K ₂ O)	0.57
Phosphorus	0.07
Arsenic	0.06

A petrographic examination of a representative sample of the pellets showed the microstructure to be predominantly cubic hausmannite (Mn₃O₄) with traces of manganous oxide (MnO), a minor portion of calcium manganate, a slag phase consisting of manganese silicate and potassium arsenate concentrated in the slag phase.

We claim:

1. A method for producing manganese oxide pellets containing not less than 48% manganese, not more than 6.0% iron, not more than 4.0% silica, not more than 7.0% alumina, not more than 1.0% alkali metals, not more than 0.12% arsenic and characterized by having a manganese to iron weight ratio of not less than about 8:1 and not more than 20:1, a porosity of 5% to 15% and a tumble index of 90% to 95%, from a manganese-bearing material which has been beneficiated to produce a manganese oxide concentrate containing about 35% to 50% manganese, about 10% to 15% iron, up to about 2.2% alkali metals, about .18% to about .25% arsenic, about 3% to about 8% water of hydration, a manganese to iron weight ratio of not more than about 7:1, substantially all the manganese particles being manganese dioxide and substantially all the iron

particles in the concentrate being non-magnetic iron oxides, said method comprising:

- roasting the manganese oxide concentrate at a temperature for a time in a reducing atmosphere to reduce substantially all the manganese dioxide particles to manganous oxide and a minor portion of manganous oxide, to reduce a major portion of the non-magnetic iron oxide particles to magnetic iron oxide particles, and to remove substantially all the water of hydration,
- magnetically separating the magnetic iron oxide particles from the non-magnetic particles in the concentrate to form a magnetic concentrate which is passed to waste and a non-magnetic concentrate,
- treating the non-magnetic concentrate to remove a substantial portion of the potassium oxide from the non-magnetic concentrate and to produce a concentrate suitable for balling,
- balling the non-magnetic concentrate,
- charging the balled non-magnetic concentrate into a furnace,
- heating the balled non-magnetic concentrate to a temperature for a time to remove a major portion but not all of the arsenic and to form pellets,
- cooling the pellets, and
- discharging the pellets from the furnace, said steps (a) through (g) being carried out under such conditions to produce said manganese oxide pellets having the aforesaid composition and physical properties.

2. The method of claim 1 wherein the roasting temperature of step (a) is between about 1100° F. and about 1600° F.

3. The method of claim 2 in which the exit gases from the roasting in step (a) contain 28-30% CO₂, 0.5-1% O₂, 0.5-1% H₂, 0.5-1% CH₄.

4. The method of claim 1 wherein the pelletizing temperature of step (f) is between about 2550° F. to about 2650° F.

5. The method of claim 1 wherein the pellets in step (g) are cooled to a temperature between about 150° F. and about 200° F.

6. A method for producing manganese oxide pellets containing not less than 48% manganese, not more than 6.0% iron, not more than 4.0% silica, not more than 7.0% alumina, not more than 1.0% alkali metals, not more than 0.12% arsenic and characterized by having a manganese to iron weight ratio of not less than 8:1 and not more than 20:1, a porosity of about 5% to about 15% and a tumble index of about 90% to about 95%, from at least one manganese-bearing material taken from the group consisting of high grade manganese oxide ore, high grade manganese carbonate ore, medium grade manganese oxide ore and medium grade manganese carbonate ore which is beneficiated to produce a concentrate containing about 35% to about 50% manganese, about 35% to about 50% manganese, about 10% to about 15% iron, up to about 2.2% alkali metals, about .18% to .25% arsenic, about 3% to about 8% water of hydration, a manganese to iron weight ratio of not more than 7:1 substantially all the iron particles in the concentrate being non-magnetic iron oxides, the method comprising:

- roasting the manganese concentrate at a temperature for a time in a reducing atmosphere to reduce substantially all the manganese compounds to manganous oxide and a minor portion of man-

ganous oxide, and to reduce a major portion of the non-magnetic iron oxide particles to magnetic iron oxide particles and to remove substantially all the water of hydration.

- b. magnetically separating the magnetic iron oxide particles from the non-magnetic particles in the concentrate to form a magnetic concentrate and a non-magnetic concentrate,
- c. discarding the magnetic concentrate,
- d. treating the non-magnetic concentrate to remove a substantial portion of the potassium oxide from the non-magnetic concentrate and to produce a non-magnetic concentrate suitable for balling,
- e. balling the non-magnetic concentrate of step (d),
- f. charging the balled non-magnetic concentrate into a furnace,
- g. heating the balled non-magnetic concentrate at a temperature for a time to remove a major portion but not all of the arsenic and to form pellets,
- h. cooling the pellets and
- i. discharging the pellets from the furnace, said steps (a) through (g) being carried out under such conditions to produce said manganese oxide pellets having the aforesaid composition and physical properties.

7. The method of claim 6 in which the roasting temperature of step (a) is about 1100° F. to about 1600° F.

8. The method of claim 7 in which the exit gases from the roasting of step (a) contain: 28-30% CO₂, 0.5-1% O₂, 0.5-1% CO, 0.5-1% H₂O, 0.5-1% CH₄.

9. The method of claim 6 in which the pelletizing temperature of step (g) is about 2550° F. to about 2650° F.

10. A method for producing manganese oxide pellets containing not less than 48% manganese, not more than 6.0% iron, not more than 4.0% silica, not more than 7.0% alumina, not more than 1.0% alkali metals, not more than 0.12% arsenic and characterized by having a manganese to iron weight ratio of not less than about 8:1 and not more than 20:1, a porosity of 5% to 15% and a tumble index of about 90% to about 95%, from a manganese-bearing material which contains cryptomelane as a portion of the manganese-bearing material, which manganese-bearing material has been beneficiated to produce a manganese oxide concentrate containing about 35% to about 45% manganese, about 10% to about 15% iron, about .18% to about .25% arsenic, about 3% to about 8% water of hydration, about 1.00% to about 2.00% potassium and has a manganese to iron weight ratio of not more than 7:1, a major portion of the manganese particles in the form of cryptomelane and a minor portion of the manganese particles in the form of manganese dioxide and substantially all the iron oxide particles being non-magnetic, the method comprising:

- a. roasting the manganese oxide concentrate at a temperature for a time in a reducing atmosphere to decompose a substantial portion of the cryptomelane to manganese dioxide and potassium oxide, reduce substantially all the manganese dioxide particles to manganous-manganic oxide and a minor portion to manganous oxide, reduce a major portion of the non-magnetic iron oxide particles to magnetic iron oxide particles and to remove substantially all the water of hydration,

- b. magnetically separating the magnetic iron oxide particles from the non-magnetic particles in the concentrate to form a magnetic concentrate and a non-magnetic concentrate,
- c. discarding the magnetic concentrate,
- d. treating the non-magnetic concentrate to remove a substantial portion of the potassium oxide from the non-magnetic concentrate and to produce a non-magnetic concentrate suitable for balling,
- e. balling the non-magnetic concentrate of step (d),
- f. charging the balled non-magnetic concentrate into a furnace,
- g. heating the balled non-magnetic concentrate to a temperature for a time to remove a major portion but not all of the arsenic and to form pellets,
- h. cooling the pellets, and
- i. discharging the pellets from the furnace, said steps (a) through (g) being carried out under such conditions to produce said manganese oxide pellets having the aforesaid composition and physical properties.

11. The method of claim 10 in which the roasting temperature of step (a) is about 1112° F. to 1598° F.

12. The method of claim 11 in which the exit gas from the roasting of step (a) contains about 28-30% CO₂, 0.5-1% O₂, 0.5-1% CO, 0.5-1% H₂, 0.5-1% CH₄.

13. The method of claim 10 in which the pelletizing temperature of step (f) is about 2550° F. to about 2650° F.

14. A method for producing manganese oxide pellets containing not less than 48% manganese, not more than 4.0% silica, not more than 7.0% alumina, not more than 6.0% iron, not more than 1.00% potassium, not more than 0.12% arsenic and characterized by having a manganese to iron weight ratio of not less than 8:1 and not more than 20:1 a porosity of about 5% to about 15% and a tumble index of about 90% to about 95%, from waste products from high grade and medium grade oxidic and carbonate ores containing manganese dioxide as a minor manganese-bearing material and cryptomelane as a major manganese-bearing material, the method comprising:

- a. beneficiating the waste products in gravity type separators to produce a manganese-bearing concentrate containing about 35% to about 50% manganese, about 10% to about 15% iron, not more than 8% silica, not more than 10% alumina, not more than 2.00% potassium, not more than .25% arsenic, about 3% to about 8% water of hydration and a manganese to iron weight ratio of not more than 7:1, a major portion of the manganese particles in the concentrate being cryptomelane and a minor portion of the manganese particles in the concentrate being manganese dioxide and substantially all the iron oxide particles being non-magnetic,
- b. roasting the manganese bearing concentrate of step (a) at a temperature for a time in a reducing atmosphere to decompose the cryptomelane to manganese dioxide and potassium oxide and to reduce substantially all the manganese dioxide particles to manganous-manganic oxide and a minor portion of manganous oxide and to reduce a major portion of the non-magnetic iron oxide particles to magnetic iron oxide particles and to remove substantially all the water of hydration,
- c. magnetically separating the magnetic iron oxide particles from the non-magnetic particles in the

concentrate to form a magnetic concentrate and a non-magnetic manganese concentrate,

- d. discarding the magnetic concentrate,
- e. treating the non-magnetic manganese concentrate to remove a substantial portion of the potassium oxide and to produce a non-magnetic manganese concentrate suitable for balling,
- f. balling the non-magnetic manganese concentrate of step (e),
- g. charging the balled non-magnetic manganese concentrate into a furnace,
- h. heating the balled non-magnetic manganese concentrate at a temperature for a time to remove a major portion but not all of the arsenic and to form pellets,
- i. cooling the pellets, and
- j. discharging the pellets.

15. The method of claim 14 in which the roasting temperature of step (b) is about 1100° F. to about 1600° F.

16. The method of claim 15 in which the exit gas from the roasting of step (b) contains 28-30% CO₂, 0.5-1% O₂, 0.5-1% CO, 0.5-1% H₂, 0.5-1% CH₄.

17. The method of claim 14 in which the pelletizing temperature of step (h) is about 2550° F. to about 2650° F.

18. In a method for producing manganese oxide pellets consisting of not less than 48% manganese, not more than 4.0% silica, not more than 7.0% alumina, not more than 1.0% alkali metals, not more than 0.12% arsenic and not more than 6.0% iron, said iron being present in a weight ratio of not less than 8 parts of manganese to one part of iron and not more than 20 parts of manganese to one part iron and characterized by a porosity of about 5% to 15% and a tumble index of 90% to 95%, from high grade, and medium grade oxidic and carbonate manganese ores, low grade oxidic and carbonate manganese ores and waste products from high grade and medium grade oxidic and carbonate manganese ore processing plants wherein said ores and waste products are beneficiated to form an upgraded manganese oxide concentrate containing about 35% to 50% manganese, about 10% to 15% iron, about .18% to about .25% arsenic, not more than about 2.00% potassium and about 3% to about 8% water of hydration which concentrate is ground, flocculated with lime, filtered, thickened, dewatered, balled and heated at an elevated temperature to form pellets, the improvement comprising treating the upgraded manganese oxide concentrate in a reduction roasting process to simultaneously reduce a substantial portion of the manganese dioxide to mangano-manganic oxide, a major portion of the non-magnetic iron oxide to magnetic iron oxide, remove substantially all the water of hydration therefrom, and to convert substantially all the insoluble potassium compounds to water soluble compounds, a substantial portion of which are removed during subsequent dewatering, and to remove a major portion but not all of the arsenic during heating at elevated temperatures to form the pellets.

19. In a method for producing manganese oxide pellets containing not less than 48% manganese, not more than 6.0% iron, not more than 4.0% silica, not more than 7.0% alumina, not more than 1.0% alkali metals, not more than 0.12% arsenic, suitable for use in manufacturing ferromanganese alloys, from the group consisting of high grade manganese ores, medium grade manganese ores and low grade manganese ores, said ores containing arsenic and potassium, in the form of insoluble potassium compounds, wherein the manganese ores are upgraded in a physical ore processing plant to produce a manganese oxide concentrate containing about 35% to 50% manganese, about 10% to 15% iron, about .18% to about .25% arsenic and about 2.00% potassium, said pellets characterized by having a porosity of 5% to 15% and a tumble index of 90% to 95%, said method comprising:

- a. roasting the manganese oxide concentrate at a temperature for a time in a reducing atmosphere to reduce substantially all the manganese dioxide (MnO₂) to manganese oxide (Mn₃O₄) and a minor portion of manganous oxide (MnO) and a major portion of the non-magnetic iron oxide (Fe₂O₃) to magnetic iron oxide (Fe₃O₄), simultaneously converting a major portion of insoluble potassium compounds therein to water soluble potassium compound, and removing substantially all the water of hydration therefrom,
- b. grinding the roasted concentrate to liberation and balling size,
- c. magnetically separating the magnetic iron oxides from non-magnetic iron oxides and manganese oxides to form a magnetic concentrate and a non-magnetic concentrate,
- d. discarding the magnetic concentrate,
- e. treating the non-magnetic concentrate to remove a substantial portion of the soluble potassium compounds and to produce a non-magnetic concentrate suitable for balling,
- f. balling the non-magnetic particles to form balls having a diameter of between about one-fourth inch to about three-fourths inch,
- g. charging the balls into a traveling grate furnace,
- h. drying the balls,
- i. heating the balls to a temperature of about 2550° F. to about 2650° F. for about one hour to form pellets, and to remove a major portion but not all of the arsenic therein,
- j. cooling the pellets to a temperature of about 150° F. to about 200° F. and
- k. discharging the pellets from the furnace, said steps (a) through (j) being carried out under such conditions to produce said manganese oxide pellets having the aforesaid composition and physical properties.

20. The method of claim 19 in which the roasting temperature of step (b) is 1112° F. to 1598° F.

21. The method of claim 19 in which the roasting temperature of step (b) is 1292° F. to 1391° F.

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