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SCUM FLOTATION OF MANGANESE DIOXIDE

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8 Claims. (Cl. 209—207)

Deposits of alluvial nature carrying a manganese content are commonly of low grade and large quantities of raw material would have to be handled in order to extract profitably the manganese values present. Attempts to treat such material on the lines of known ore beneficiation methods have not been very successful as the efficiency is low and the cost high. I have now discovered that the manganese values in such materials can be extracted in a relatively simple manner with relatively cheap treating agents. Other objects and advantages will appear from the following description.

To the accomplishment of the foregoing and related ends, said invention then comprises the features hereinafter fully described and particularly pointed out in the claims, the following description setting forth in detail certain illustrative embodiments of the invention, these being indicative, however, of but a few of the various ways in which the principle of the invention may be employed.

The raw material or source material for the present process is manganese-containing deposits such as bog manganese, "wad" type of manganese ore and the like, the general characteristic being gravel or sand-like particles having a coating of pyrolusite and/or other manganese compounds. Of such deposits in the United States, some contain up to 30 per cent of manganese, but usually the content is much less. The core particles of the grains are usually silica. With the manganese compounds there may be varying amounts of iron oxide, calcium and aluminum compounds, etc. With material of such character, it is possible by my process to produce a manganese concentrate of a grade suitable for battery use, for making ferro-manganese, and for other uses.

The raw material is usually conditioned for operation by initial grinding. Such reduction may be in the ranges of 20 to 250 mesh fineness. Preliminary to the grinding it may in some cases be desirable to submit the material to a screening in order to eliminate any pieces of wood and other undesirable materials.

Some ores contain an undesirable amount of iron, which may be removed or reduced at this or a later stage of the process. If the iron is in the form of magnetic oxide, it may be removed by magnetic separation. If it is in the form of non-magnetic oxide the magnetic separation may be preceded by roasting in a reducing atmosphere, so as to convert the oxides to the magnetic form.

The finely ground material is made into a slurry with water and ammonia. Ammonium hydroxide of 26° stock is supplied at a rate in the range of 2 to 20 pounds per ton of ore and a desirable proportion for the slurry is in the range of 1 to 3 tons of water solution per ton of material. That is, as 26° stock ammonium hydroxide is 28% NH_3 the concentration of the working solution is dilute, or at most under .3%. Generally, around 20 pounds of 26° stock ammonia per ton of material is satisfactory. Such ammoniated water is largely returned from a later stage of the process and reused.

Although the fineness of the grinding should be such, that there is a nearly complete separation of the particles of iron oxide and manganese oxide from the gangue, still there will always be a certain amount of such oxides adhering to particles of the gangue, and I have found that the ammonia has a loosening or freeing effect on the bond between the components. For this reason I have found it beneficial to let the material remain in this soaking zone for some time, or up to 60 minutes, and with sufficient agitation to prevent settling. The treatment may be carried out at ordinary temperature or preferably at elevated temperature within the limits in which ammonia is not greatly lost by being driven off. Temperatures up to around 180° F. are generally satisfactory. The slurry from the preliminary mixing is then subjected to vigorous agitation. This may be in one stage, or in a number of stages. Usually mechanical agitation is desirable, but air agitation can be applied. After the vigorous agitation in the ammonia solution, the slurry is run into a settling basin, where it may remain up to about three minutes.

After the vigorous agitation, the slurry in the settling basin shows a differential separation, the manganese compounds floating to the surface as a scum or slime while the gangue sinks to the bottom. From the settling zone the scum or slime-froth is floated off at the top. Such scum may be taken off at any stage, including the very first, when it is feasible. Any suitable means for a more or less continuous discharge of the gangue tailings may be employed at the bottom, such as a helicoidal screw discharger or other means.

In one convenient form of arrangement, there may be a number of agitated sections each feeding to the next, and a settling basin section, all in a connected cell series, the manganese oxide slime overflowing continuously from the top of the settling basin, and the gangue being continuously removed from the bottom. The gangue, with or without additional washing, may be discarded. The concentrated manganese dioxide slime as taken from the top of the settling zone is generally of a purity such as to grade directly for further uses. If for making ferro-manganese, the manganese concentrate as taken from the top of the settling zone can be de-watered and then sintered or nodulized.

As an example: Material on the order of manganese wad with low iron content is run through a coarse screening and is then ground to about 200 mesh. The finely ground material is made into a slurry with water and 5 pounds of 26° NH_4OH per ton of water, and 2 parts of such solution to one part of the ground material, the temperature of the solution being 180° F. From the soaking zone the slurry is passed to the first agitating zone where it is vigorously agitated for about 5 minutes, then it is passed on to a second agitating zone where this operation is repeated, and thence it proceeds to a settling zone, where a separation takes place, the manganese compound going to the surface as a scum which is taken off by an overflow at the top, and the finely divided gangue settling to the bottom is taken off by a screw discharger.

It is surprising that such a separation is effected by ammonia. The nature of the action is obscure, and it is difficult to explain on the basis of the known chemical and physical conditions. Even if air should be the means applied for agitation rather than mechanical agitation, the action is not a typical flotation action, and it is remarkable that a heavy specific gravity material, the manganese dioxide, should come to the top, and in such highly purified form. A particularly favorable result also from such agent as ammonia, is that it is a volatile agent and ultimately leaves the manganese dioxide product clean.

The term "manganese oxide concentrate" used in the following claims for conciseness includes various proportions of manganese compounds such as pyrolusite, psilomelane, braunite, manganite, etc., and impurities such as iron oxide, alumina, silica, calcium, magnesium, etc.

Other modes of applying the principle of the invention may be employed, change being made as regards the details described, provided the features stated in any of the following claims or the equivalent of such be employed.

I therefore particularly point out and distinctly claim as my invention:

1. In the production of manganese oxide concentrates, freeing manganese oxide from associated finely ground gangue by agitation with an ammonia solution whose concentration does not exceed the equivalent of adding twenty pounds of 26° stock ammonia to a ton of water.

2. In the production of manganese oxide concentrates, agitating finely ground ore carrying manganese oxide in 1–3 times its weight of warm ammonia solution whose concentration does not exceed the equivalent of adding twenty pounds of 26° stock ammonia to a ton of water, freeing and raising manganese oxide to the surface of the solution as a scum, and taking off the manganese oxide concentrate scum.

3. In the production of manganese oxide concentrates, slurrying finely divided ore containing manganese oxide with 1–3 times its weight of ammonia solution whose concentration does not exceed the equivalent of adding twenty pounds of 26° stock ammonia to a ton of water, agitating, then settling, and freeing and raising manganese oxide to the surface of the solution as a scum.

4. In the production of manganese oxide concentrates, making a slurry of ore containing manganese oxide with ammonia solution whose concentration does not exceed the equivalent of adding twenty pounds of 26° stock ammonia to a ton of water, subjecting the slurry in succession to soaking with agitation, vigorous agitation, settling, and freeing and raising manganese oxide to the surface of the solution as a scum, while the gangue sinks as sediment at the bottom, and returning ammonia solution to the soaking zone.

5. In the production of manganese oxide concentrates, the combination of steps of separating magnetic iron oxide in a magnetic separating zone from a finely divided ore carrying manganese oxide and iron oxide, mixing the manganese-containing remainder with ammonia solution whose concentration does not exceed the equivalent of adding twenty pounds of 26° stock ammonia to a ton of water, agitating, then settling, and separating the manganese oxide concentrate at the top of the solution and the gangue at the bottom.

6. In a process according to claim 5, roasting the ore if iron oxide contained is non-magnetic and converting such into magnetic oxide, and magnetically separating the same.

7. A process for the production of manganese oxide concentrates, which includes the combination of steps of slurrying finely divided manganese ore with an aqueous solution of ammonia whose concentration does not exceed the equivalent of adding twenty pounds of 26° stock ammonia to a ton of water, agitating, and freeing and raising manganese oxide to the surface of the solution, and collecting the gangue at the bottom as a residue.

8. A process for the production of manganese oxide concentrates from manganese ore of varying degree of fineness, comprising mixing the ore with an aqueous solution of ammonia whose concentration does not exceed the equivalent of adding twenty pounds of 26° stock ammonia to a ton of water, agitating, and removing the concentrate from the top of the solution and the gangue from the bottom.

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