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REFRACTORY MATERIAL AND METHOD OF MANUFACTURING

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This invention relates to a basic refractory material suitable for use in lining furnaces, and to a method of manufacturing the same, and applies more particularly to a lining material manufactured from burned dolomite, limestone, magnesite, or the like.

The material is especially adapted for repairing linings of open hearth, electric and similar furnaces. The refractory material, suitably sized, is thrown into the hole in the furnace lining and is "baked" by the furnace heat to convert the repair material into a hard mass substantially integral with the original lining, which remains in place and is not washed out by the subsequent charges. Material for this purpose besides being resistant to temperature and chemical attack under the conditions of its use should have characteristics such that the entire mass is penetrated by the heat and converted into a hard refractory. The material should accordingly be of such particle size and physical condition as to permit the heat to readily penetrate the mass, as otherwise a hard crust would be formed on the surface while the material below the crust would remain in the original loose condition and would be washed out of the hole as soon as the crust became broken. Since, in commercial practice, repair material may frequently be kept in storage for long periods, it should be highly resistant to attack by moisture or other causes and to breakage in handling.

In accordance with the present invention dolomite, limestone, magnesite, or the like, is so treated as to cause the resultant product to have the above mentioned characteristics.

The invention also consists in forming a product having the general characteristics, the new and useful applications, and the several original features of utility hereinafter set forth and claimed.

Although the novel features which are believed to be characteristic of this invention will be particularly pointed out in the claims appended hereto, the invention itself, as to its objects and advantages, and the manner in which it may be carried out, may be better understood by referring to the following description in which certain specific disclosures are made for purpose of explanation. It will be understood, however, that the processes and the steps thereof may be modified in various respects without departing from the broad aspects of the invention.

In carrying out the present invention the raw material, such as dolomite, may be crushed, if necessary, to pass a screen having approximately ¼" openings. The size of particles need not be closely limited, but fine grinding is unnecessary while crushing to comparatively coarse sizes reduces power consumption and lessens the amount of dust with consequent easier and better working conditions in the plant, and facilitates the control of the subsequent operations.

Natural dolomite rock usually contains impurities, such as silica, iron and alumina, which act in the nature of a flux for the refractory and tend to reduce the melting point thereof. For most refractory uses a small percentage of these impurities is desirable, although the proportions should be held within definite limits in order to obtain a suitable control of the break-down point of the dolomite and also, in certain uses, to assure desired chemical reactions between the metal of the charge and the lining.

The refractory should preferably have a sufficiently high melting point to prevent appreciable softening under furnace operating conditions and at the same time the melting point should be sufficiently low to permit the refractory to be baked in place at temperatures not too greatly above the normal operating temperatures of the furnace. The material should also be resistant to erosion and usually to chemical attack by the furnace charge, although in special instances it may be employed to assist chemically in the removal of impurities from the bath.

In carrying out the present invention, a raw material should be used which does not contain excessive proportions of harmful impurities. For example, for making a dolomite refractory for lining basic open hearth steel furnaces where silica is objectionable, dolomite stone should preferably be used which will make a product with less than 7% of silica, although the content of iron oxide may be substantially higher. Consequently, if the dolomite is deficient in the required fluxes, suitable fluxes may be added and in these additions due regard should be had as to the use to be made of the refractory. In the above example, if the rock were deficient in fluxes, iron oxide would be added in the form of iron ore or mill scale in sufficient quantities to bring the iron oxide content of the mixture to say 5% to 10%, equivalent to approximately 10% to 20% in the product. Obviously, in preparing refractory material for other uses, a suitable oxide flux would be selected.

Flux material should preferably be added in as fine or finer particles than the original stone so

that it may be thoroughly distributed throughout the mass.

It is also necessary to employ a proportion of solid fuel or reducing agent which may be crushed to a size similar to or finer than the stone and mixed therewith in a suitable manner. Various materials, such as coke breeze, anthracite or bituminous fines, retort coke and the like, may be employed depending upon their availability and cost. In general from 10% to 20% of fuel and reducing agent would be sufficient, although these figures may vary widely depending upon various factors, such as the B. t. u. value, ash content, etc., of the material. Usually a smaller proportion of anthracite or coke breeze would be required than of bituminous coal since the volatile matter of the latter may be partially lost by distillation in the process.

The crushed stone, such as dolomite, together with the fluxes and fuel, as above mentioned, are preferably treated to obtain a thorough mixture and intermingling of the various particles. Return fines from previously heated charge, may also be added to the mixture if desired, as will be hereinafter pointed out. The mixture is then carefully moistened with a limited amount of water which is uniformly distributed throughout the mixture. Only sufficient water is added to moisten slightly all of the particles so that the mixture when lightly squeezed in the hand will retain its shape, care being taken not to form a mud, slime or slurry. Properly moistened the charge particles adhere lightly together in a loose, air-permeable mass, the finer particles being attached to the coarser, but without collecting in the form of lumps or chunks and with considerable void spaces throughout the mass.

After the material has been thoroughly mixed and moistened it is spread uniformly in a thin pervious layer and the fuel in the mixture is ignited as by temporary application of a flame to the top surface. Thereafter, a blast of air is drawn through the layer which maintains the combustion of the fuel and causes the combustion to travel downwardly through the entire bed. This may be accomplished on any desired apparatus, such as a sintering machine having perforated pallets which are adapted to contain a thin charge of material. In a particular instance 15 minutes was sufficient to burn out the fuel in a 5 inch bed of charge, the combustion as a whole beginning at the top surface and rapidly progressing downwardly through the bed.

By reason of the intense heat created by this highly forced combustion of the fuel intermixed with the charge, the material is raised to a high temperature such that not only are the carbonates decomposed but also the various fluxing agents present naturally or by addition, probably affected also by the reducing effect of the incandescent carbon and carbon monoxide from the burning fuel in contact with them, react with the liberated lime and magnesia, fusing and forming compounds which fuse together the particles originally adjacent, whereupon the cold air currents following cool and freeze the molten particles before they have time to flow together sufficiently to block off the air passage.

It is not known certainly whether the fluxes unite with all lime and magnesia, or whether compounds are formed with part of these with which the remainder remains in solid solution, or just what exact chemical change is effected, but the result is that the mass, originally made up of innumerable individual particles of stone, flux and fuel and having somewhat the appearance of fine gravel, becomes largely converted to what may be called a fusion product in which the original character has disappeared and the particles have been more or less completely fused to form new compounds and have been transformed physically to a dark colored porous cellular cake. This cake as a whole is rather weak and brittle, breaking down to comparatively small fragments which themselves are still for the most part irregular in shape and cellular in character but are hard and strong compared to the cake as a whole. This is due largely to the fact that the bed of material undergoes a heavy shrinkage in volume which results, not in a contraction of the mass as a whole (which would produce a much thinner, relatively solid cake), but in innumerable series of local contractions as the adjacent particles, under the influence of the intense heat locally developed, shrink and fuse together to form small irregular cellular bodies which are attached to one another by smaller bodies and with very considerable pores or open spaces between them. Thus while the cake as a whole is relatively weak, when it has once been broken up the resulting fragments themselves are strong. In places throughout the cake there may appear occasional calcined fragments of the larger particles of stone which cooled before being absorbed in the fused mass, and also occasional grayish patches of calcined but unfused material, these latter the result of insufficient temperatures which may have been caused by undue packing of the bed at these points or other irregularity in carrying out the operation. Properly conducted, the operation will produce little of this, however.

The cellular particles aforementioned are well suited for some purposes and may be used either as produced or after crushing and screening to required size, for it will be understood that differently sized material may be required for different uses. Or if desired, the larger particles may be screened out for use and the fines may be mixed with more stone, fuel, etc. to form part of the next charge.

The returned fines materially assist the operation by shortening the time required and producing a somewhat stronger product. These particles form nuclei for the reactions about which the fresh particles react more readily while the unfused calcined lime and magnesia assist in producing a permeable bed of material, possibly by bonding together the moistened particles of stone and flux. For example, it has been found that under certain conditions, especially where a strong draft is used with a charge containing a large proportion of fine material and where the grate bars are worn so that the openings have become enlarged, there may be a tendency for the charge to fall through the grates in spots, forming blowholes, but if a small proportion of previously treated material is mixed with the charge this tendency is overcome and the charge may be burned without the formation of blowholes even under strong draft.

When the above process is applied to dolomite the resultant material may be crushed to size and applied to certain uses, such as the formation of furnace linings. For some purposes, however, the product may consist of too small particles or may be insufficiently strong or unsuitable for other reasons. In such a case the material may be treated further, as described below, to produce a stronger cake. In treating limestone and magnesite it is also frequently found necessary to

give the second treatment outlined below inasmuch as the same may not be completely fused in the treatment above mentioned and the product may not have the desired characteristics.

In this further treatment, the product from the first operation, preferably as a whole, may be crushed to pass a quarter inch opening screen, and a small proportion of fuel added, as before. Less fuel will ordinarily be required since decomposition of the carbonates has already been effected and heat for fusion only is necessary, so that in general 5% to 15% of fuel will be sufficient.

Addition of fluxes will preferably have been made in the first operation, but if the chemical composition of the material is for any reason unsatisfactory, suitable adjustment may be made by appropriate additions to the mixture. The various ingredients may then be thoroughly mixed and moistened as before described, and the prepared charge spread in a uniform permeable bed, ignited, and the fuel burned out, much as in the first operation. In this second treatment, however, the bed will usually be more air-permeable, owing to the structure of the retreated material and a deeper bed may be formed without presenting undue resistance to the draft. Combustion is even more rapid (10 to 15 minutes time for a five inch bed) and intense heat is developed in spite of the decreased amount of fuel present, resulting in momentary fusion of the particles and the production of a cellular porous cake, somewhat similar to the first product but thicker walled, more massive and considerably stronger as a whole. In general the lower portion of the cake will be tougher and more massive than the upper, as a result of the mass accumulation of heat and because the heat from the igniting flame (2600–3000° C.) even when using a large oil burner, is less than that from the highly forced combustion of the fuel intermixed in the charge.

This cake may be produced in pieces too large for most uses, in which case it may be crushed and separated into the desired sizes. The crushed product contains magnesium and calcium oxides and possibly other compounds fused with a flux to form a mass of dark colored, sharp edged, irregular shaped, cellular fragments. It is highly resistant to attack by moisture and may be stored indefinitely, even in the open, without substantial deterioration. Pieces kept under water and heaps standing in the open exposed to rain for weeks have remained unaffected except for the appearance of a slight whitish efflorescence.

When used for patching holes in open hearth furnace linings, this new refractory material has been found to hold its place in the spot where it is thrown even on steep banks, while, due to its open structure, the heat rapidly penetrates the mass and bakes it into a unified part of the furnace lining. Its effectiveness as a refractory is shown by successful use in lining electric furnaces for the refining of steel, where material made by the hereindescribed process from dolomite base has proven satisfactory under conditions where other dolomite refractory materials have failed, and with a greatly decreased consumption of refractory per ton of steel produced.

The following examples of carrying out the above described process are given for purposes of illustration only:

(1) Dolomite analyzing approximately 92% calcium and magnesium carbonates, 4% silica and 4% iron oxide and alumina was crushed to pass a four mesh screen, mixed with 15%–20% anthracite fines (No. 5 buckwheat) moistened as above described and deposited in a five inch depth bed on the grates of a continuous Dwight-Lloyd sintering machine. The top surface was ignited by flame from an oil burner and the fuel burned out under forced draft of 8 inches (water gauge), this requiring fifteen minutes time. The product was a black cellular cake, which on being discharged from the grates broke up into fragments approximately one inch in size and finer. This product was crushed to pass one half inch mesh screen, and the coarser particles (plus 8 mesh) were found to be satisfactory for use.

(2) Dolomite analyzing approximately 98% calcium and magnesium carbonates, 1¼% silica and 1¾% iron oxide and alumina was crushed to pass four mesh screen, mixed with 5%–15% ground basic open hearth slag and 10%–20% coke breeze. The mixture was moistened, placed on the grates of a sintering machine in a five inch depth bed, ignited and the coke burned out under forced draft of 6 inches (water gauge) in 20 minutes time, resulting in a blackish friable cellular cake with a small amount of grayish unfused product. This cake was crushed to pass a ¼ inch screen, mixed with 10–15% coke breeze, moistened and again burned under forced draft, requiring 12 minutes time. The product, a strong cellular cake black in color, was crushed to half inch particles for use.

(3) Dolomite of the same composition as in the second example was crushed to pass a ⅜ inch screen, mixed with 4%–10% fine mill scale and 10%–20% coke breeze, moistened, placed on the sintering machine in a five inch depth bed, ignited and burned under forced draft of 6 inches water gauge, the time being twenty minutes. The product was a friable cellular cake mostly black but with a small amount of grayish calcined but unfused product. This was all crushed to pass a ¼ inch screen, mixed with 10–15% coke breeze, moistened and again burned (requiring 10 minutes), resulting in a firm strong cake which was all crushed to a half inch for use.

(4) High calcium limestone was crushed to pass a $\frac{3}{16}$ inch screen, mixed with 5%–10% of iron ore and 15%–25% of coke, moistened and placed on a sintering machine in a 5 inch bed, ignited and burned in about 20 minutes. The product was crushed to pass a $\frac{3}{16}$ inch screen and 10%–15% of coke added, moistened and again sintered in a 5 inch bed, requiring about 10 minutes for complete burning. The product was then crushed for use. It was more highly refractory than the corresponding dolomite base product, but was not as resistant as the latter, breaking down to some extent into smaller particles after open storage for four weeks. The high calcium base refractory should preferably be stored in an air tight container, such as paper bags, until used. However, if a somewhat increased proportion of suitable fluxes is used, as compared with dolomite base refractory, the product resists weathering satisfactorily while still being relatively more refractory.

The hereindescribed method for producing this refractory material is simple to practice, is readily adaptable either to continuous or batch production, requires little attention, and is exceedingly rapid in operation, requiring only a few moments burning time.

What I claim is:

1. The process of manufacturing refractory material which comprises forming a thin, porous layer containing an intimate mixture of mate-

rial selected from the group consisting of dolomite, magnesite and limestone, together with fuel and flux in predetermined proportions, said material having a moisture content such that the particles adhere lightly together and form a permeable mass, igniting the fuel at one surface of the layer and rapidly burning the fuel by passing air currents through the mass at a rate which develops intense heat sufficient to momentarily fuse substantially all of the individual particles and transform the layer into a coarse cellular cake.

2. The process of manufacturing refractory material which comprises forming a thin, porous, adherent, air permeable layer containing an intimate mixture of material selected from the group consisting of dolomite, magnesite and limestone, together with a predetermined proportion of fuel, igniting the fuel at one surface of the layer and rapidly burning the fuel by passing air currents through the mass at a rate which develops intense heat sufficient to momentarily fuse substantially all of the individual particles and transform the layer into a coarse cellular cake.

3. The process of manufacturing refractory material which comprises forming a thin porous layer of crushed dolomitic material, together with fuel and flux in predetermined proportions, said material having a moisture content such that the particles adhere lightly together and form a permeable mass, igniting the fuel at one surface of the layer and rapidly burning the fuel by passing air currents through the mass at a rate which develops intense heat sufficient to momentarily fuse substantially all of the individual particles and transform the layer into a coarse cellular cake.

4. The process of manufacturing a refractory from a self-fluxing material containing any of dolomite, magnesite and limestone, and carbonaceous material in intimate admixture which comprises moistening said mixture to a consistency such that the particles adhere lightly together and form an air permeable mass, spreading the mixture in a thin layer, igniting the fuel at one surface of the layer and rapidly burning the fuel by passing air currents through the mass at a rate which develops intense heat sufficient to momentarily fuse substantially all of the individual particles and transform the layer into a coarse cellular cake.

5. The process of manufacturing a refractory material from a self-fluxing material containing any of dolomite, magnesite and limestone, which comprises finely dividing said material and adding thereto carbonaceous material in predetermined proportion, thoroughly mixing the ingredients in the presence of moisture such that the particles adhere lightly together and form an air permeable mass, spreading the mixture in a thin layer, igniting the fuel at one surface of the layer and rapidly burning the fuel by passing air currents through the mass at a rate which develops intense heat sufficient to momentarily fuse substantially all of the individual particles and transform the layer into a coarse cellular cake, crushing the resultant cake and returning the fines to subsequent charges for speeding the operation and assisting the formation of an air-permeable mass.

6. The process of manufacturing a refractory material from material selected from the group consisting of dolomite, magnesite and limestone, which comprises finely dividing said material and adding thereto flux and carbonaceous material in predetermined proportions, thoroughly mixing the ingredients in the presence of moisture such that the particles adhere lightly together and form an air permeable mass, spreading the mixture in a thin layer, igniting the fuel at one surface of the layer and rapidly burning the fuel by passing air currents through the mass at a rate which develops intense heat sufficient to momentarily fuse substantially all of the individual particles and transform the layer into a coarse cellular cake, crushing the resultant cake and returning the fines to subsequent charges for speeding the operation and assisting the formation of an air-permeable mass.

7. The process of manufacturing a refractory from dolomitic material, which comprises crushing said material to approximately ¼ inch size and adding thereto from 5% to 15% of slag and from 10% to 20% of finely divided coke, thoroughly mixing the ingredients and moistening to a consistency such that the particles adhere lightly together and form a permeable mass, spreading the mixture in a thin layer, igniting the fuel at one surface of the layer and causing rapid combustion of the fuel by passing air currents through the mass at a rate sufficient to produce intense heat and fuse the particles together in a coarse cellular cake.

8. The process of manufacturing a refractory from dolomitic material passing a ¼ inch screen, which comprises adding thereto approximately 4% to 10% of iron oxide and 10% to 20% of finely divided solid fuel, thoroughly mixing the ingredients and moistening to a consistency such that the particles adhere lightly together and form a permeable mass, spreading the mixture in a thin layer, igniting the fuel at one surface of the layer and causing rapid combustion of the fuel by passing air currents through the mass at a rate sufficient to produce intense heat and fuse the particles together in a coarse cellular cake.

9. The process of manufacturing a refractory from a self fluxing material containing any of dolomite, magnesite and limestone, which comprises finely dividing said material and adding thereto carbonaceous material in predetermined proportions, thoroughly mixing the ingredients in the presence of moisture such that the particles adhere lightly together and form an air-permeable mass, spreading the mixture in a thin layer, igniting the fuel at one surface of the layer and causing rapid combustion of the fuel by passing air currents through the mass at a rate sufficient to produce intense heat and momentarily fuse the particles, crushing the product, adding further quantities of fuel and moisture, mixing and spreading the mixture in a thin layer and repeating the above treatment to produce a porous cellular cake having comparatively large particles and of substantial strength, and crushing the cake to form a refractory material suitable for furnace linings.

10. The process of manufacturing a refractory from magnesia bearing material, which comprises finely dividing said material and adding thereto carbonaceous material in predetermined proportions, thoroughly mixing the ingredients in the presence of moisture such that the particles adhere lightly together and form an air-permeable mass, spreading the mixture in a thin layer, igniting the fuel at one surface of the layer and causing rapid combustion of the fuel by passing air currents through the mass at a rate sufficient to produce intense heat and momentarily fuse the particles crushing the product, adding

further quantities of fuel and moisture, mixing and spreading the mixture in a thin layer and repeating the treatment to produce a porous cellular cake having comparatively large particles and of substantial strength and crushing the cake to desired size.

11. The process of manufacuring a refractory from magnesia bearing material, which comprises forming a thin layer of a mixture of said material and flux and carbonaceous material, together with previously treated fines in the presence of moisture such that the particles adhere lightly together and form an air-permeable mass, igniting the fuel at one surface of the layer and causing rapid combustion of the fuel by passing air currents through the mass at a rate sufficient to produce intense heat and momentarily fuse the particles, crushing the product, removing fines for return as above, adding further quantities of fuel, mixing and spreading the mixture in a thin layer and repeating the treatment to produce a porous cellular cake having comparatively large particles and of substantial strength and crushing the cake to desired size.

12. The process of manufacturing refractory material from limestone, which comprises crushing said material to approximately $\frac{3}{16}$ inch size and adding thereto about 5% to 10% of iron oxide bearing material and about 15% to 25% of finely divided coke, thoroughly mixing the ingredients and moistening to a consistency such that the particles adhere lightly together and form a permeable mass, spreading the mixture in a thin layer, igniting the fuel at one surface of the layer and causing rapid combustion of the fuel by passing air currents through the mass at a rate sufficient to produce intense heat and momentarily fuse the particles, crushing the product to about $\frac{3}{16}$ inch size, adding about 10% to 15% of finely divided coke, moistening and mixing the material and spreading the mixture in a thin layer and repeating the treatment to produce a porous cellular cake having comparatively large particles and of substantial strength.

13. The process of manufacturing a refractory from dolomitic material passing a ¼ inch mesh screen, which comprises adding thereto approximately 4% to 10% of iron oxide and 10% to 20% of finely divided solid fuel, thoroughly mixing the ingredients and moistening to a consistency such that the particles adhere lightly together and form a permeable mass, spreading the mixture in a thin layer, igniting the fuel at one surface of the layer and causing rapid combustion of the fuel by passing air currents through the mass at a rate sufficient to produce intense heat and momentarily fuse the particles, crushing the product to approximately ¼ inch size, adding 10% to 15% of fuel, moistening and mixing the material and spreading the mixture in a thin layer and repeating the heat treatment to produce a porous cellular cake having comparatively large particles and of substantial strength, and crushing the cake to produce a refractory material suitable for furnace linings.

14. A refractory comprising material selected from the group consisting of dolomite, magnesite and mestone and a flux calcined and fused together in the form of irregular cellular fragments of substantially uniform composition.

15. The process of manufacturing refractory material which comprises forming a thin porous layer of crushed magnesia bearing material, together with fuel and flux in predetermined proportions said material having a moisture content such that the particles adhere lightly together and form a permeable mass igniting the fuel at one surface of the layer and rapidly burning the fuel by passing air currents through the mass at a rate which develops intense heat sufficient to momentarily fuse substantially all of the individual particles and transform the layer into a coarse cellular cake.

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