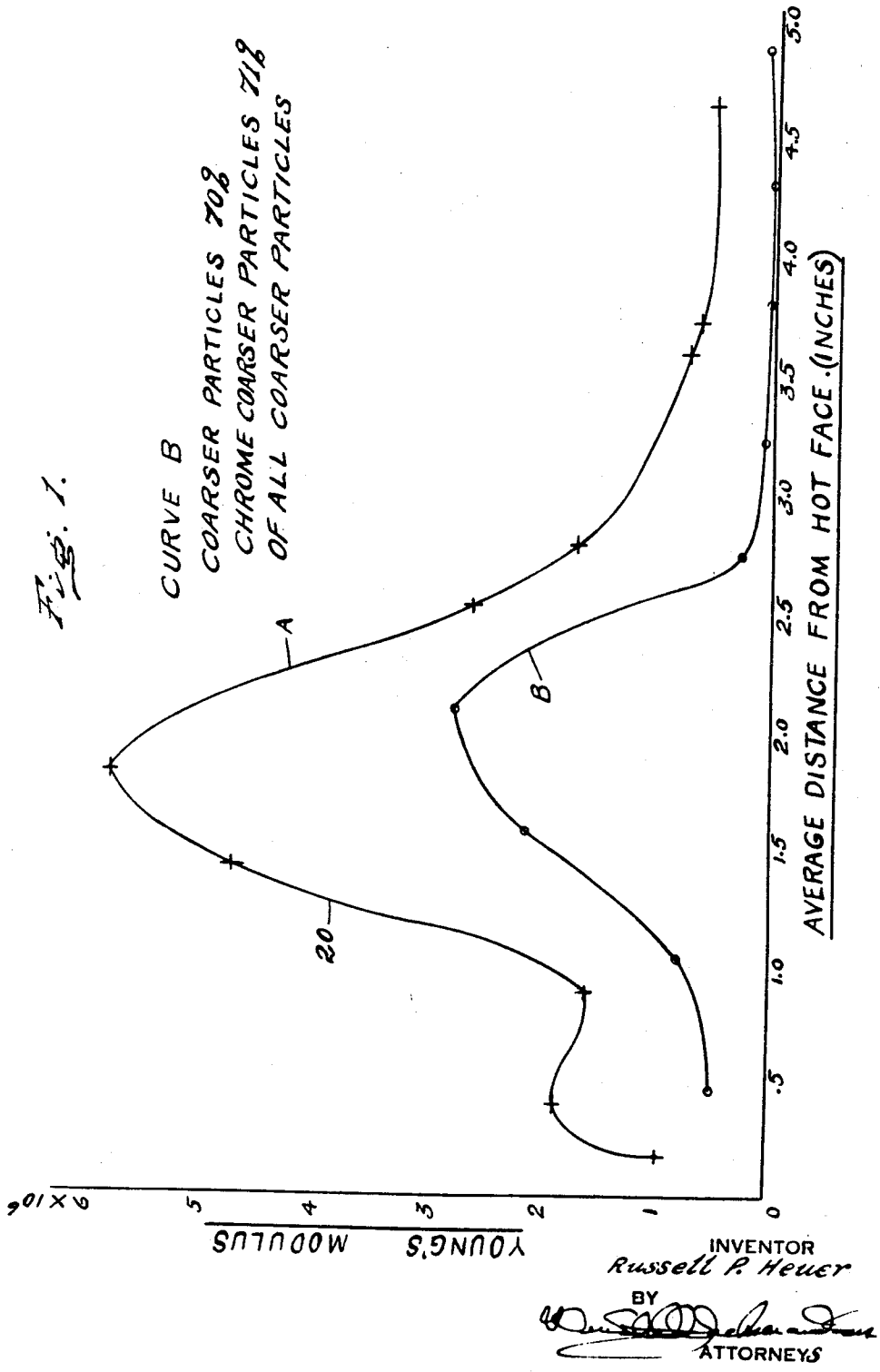
May 29, 1962 R. P. HEUER 3,036,925

BASIC REFRACTORY BRICK

Filed Oct. 13, 1958

2 Sheets-Sheet 1



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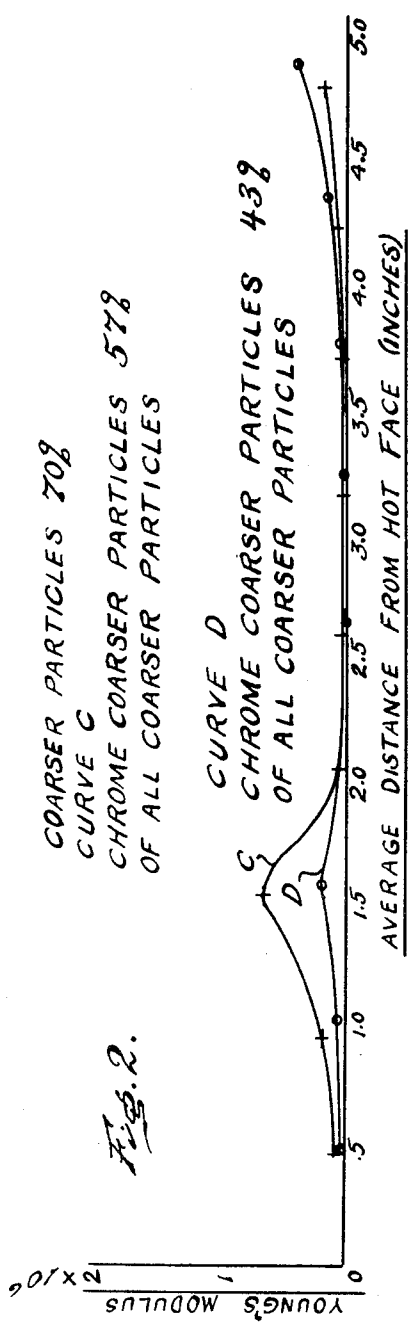


Fig. 2.

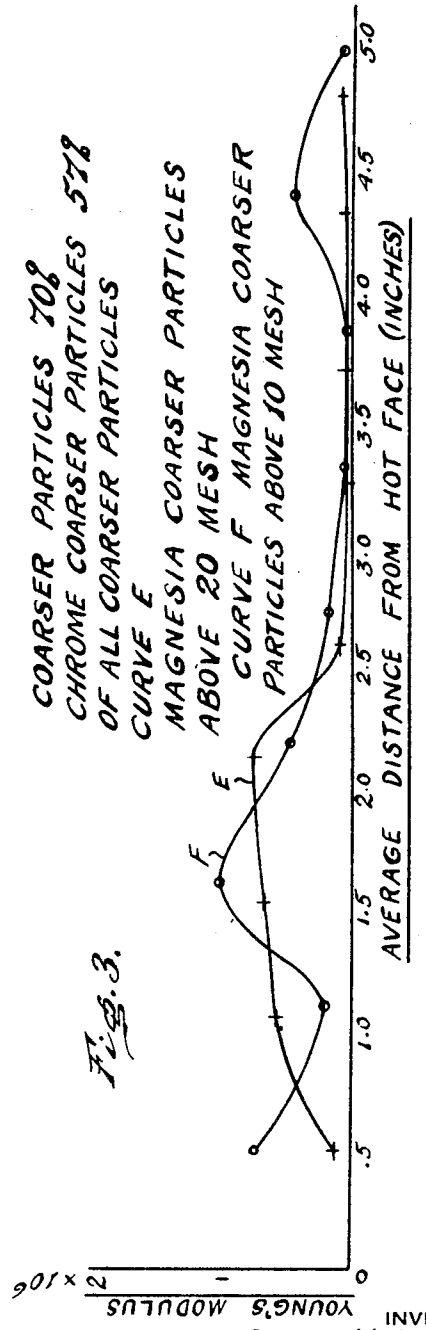


Fig. 3.

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BASIC REFRACTORY BRICK

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5 Claims. (Cl. 106—59)

The present invention relates to basic refractory brick suitable for use without kiln firing and made from mixtures of dead burned magnesia (including fused magnesia) and chrome ore.

The present application is a continuation-in-part of my application Serial No. 523,800, filed July 22, 1955, for Basic Refractory Brick, now abandoned, of my application Serial No. 582,467, filed May 3, 1956, for Basic Refractory Brick, now abandoned, and of my application Serial No. 728,984, filed April 16, 1958, for Basic Refractory Brick, now abandoned.

A purpose of the invention is to improve the resistance of such brick to spalling and destruction under the action of forces which would otherwise cause large segments at the hot face of the brick to become detached due to internal cracks which form in the brick during use.

A further purpose is to restrict the relation of proportions and size ranges of the coarser particles of a basic refractory brick within a range which will be more tolerant of silicate migration than the brick of the prior art and less susceptible to internal cracking.

A further purpose is to increase the resistance of such brick to the formation of internal cracks near the hot face which are associated with the migration of silicate impurities inward from the hot face with resultant concentration in the region where internal cracks develop.

A further purpose is to produce such brick with an internal structure able to tolerate the effects of silicate migration with a minimum of internal cracking, preferably by adjusting the particle size of the brick to obtain a low Young's modulus in the region which is particularly susceptible to cracking.

A further purpose is to produce a refractory brick, unfired and suitable for use without kiln firing, which has improved resistance to cracking, the brick being composed of a bonding substance of the character later explained and refractory material composed of a mixture of coarser magnesia particles, coarser chrome ore particles and finer magnesia particles, unnaturally low in particles of intermediate size, the coarser particles being of a size so that more than 90 percent of the coarser particles by weight rest on a 28 mesh screen, more than 80 percent of the coarser particles by weight rest on a 14 mesh screen, and more than 35 percent rest on an 8 mesh screen, in the preferred embodiment the coarser particles being smaller than 4 mesh, the coarser particles making up 65 to 90 percent by weight of the refractory material, 10 to 50 percent by weight of the refractory material being coarser chrome ore particles, the finer particles being smaller than 48 mesh, making up 10 to 35 percent by weight of the refractory material, substantially free from chrome ore.

A further purpose is to produce a basic refractory brick of the type just mentioned, in which the coarser particles other than the chrome ore particles mentioned are substantially all magnesia particles smaller than 4 mesh.

A further purpose is to provide a refractory brick which is capable of resisting the combined attack of migrating silicates which cause cracking in a brick containing chrome ore and magnesia, and simultaneously to provide such a brick with a proper content of magnesia to form magnesio-ferrite spinel with iron oxide taken up by the refractory during the furnace operation, thereby providing a refractory which can tolerate the high absorption of iron oxide and still resist both fusion at highest furnace temperature and formation of damaging cracks.

A further purpose is to provide a refractory brick of the character described with steel plates comolded in the internal structure of the brick and/or on the external surface of the brick as illustrated for example in Heuer and Fay, U.S. Patent No. 2,652,793, granted September 22, 1953, for Refractory Furnace Roof Brick Resistant to Spalling.

Further purposes appear in the specification and in the claims.

The curves plot as ordinate Young's modulus (to be multiplied by 10^6) and as abscissa average distance from the hot face in inches.

Basic refractory brick made from dead burned magnesite or fused magnesite, sometimes called periclase, and hereinafter referred to as dead burned magnesia, mixed with chrome ore, have been widely used in the construction of metallurgical and other furnaces and especially in roofs, walls, hearths, downtakes and other structure of basic open hearth furnaces. Such brick may be burned in kilns before use or may be used without burning if a suitable chemical bond is provided which develops the desired physical property without burning.

Unburned refractory of this character have been described in my U.S. Patents No. 2,443,424, granted June 15, 1948, for Brick Having Low Modulus Rupture, and No. 2,087,107, granted July 13, 1937, for Chrome Magnesia Refractory and Method. In my U.S. Patent No. 2,289,911, granted July 14, 1942, for Refractory Brick Structure, I have also described unburned brick which are provided with external sheet steel spacer plates comolded in position. These brick have been found in many instances to be more resistant to spalling than kiln fired brick. Such brick provided with metallic spacer plates are used in furnace walls, roofs and flues and are particularly well suited to so-called suspended construction.

I have found, however, particularly in the case of roof construction, that the bricks used have a tendency to develop internal cracks parallel to the hot face of the roof, about one inch or two inches away from the hot face. These cracks cause the heated end to detach itself from the brick and they therefore greatly accelerate the failure of the brick. I have previously discovered that comolding of internal metallic spacer plates extending perpendicular to the hot face produces a brick of minimum cracking tendency, but even with this improvement cracking an inch or two from the hot face still occurs.

It is believed that there may be a number of factors which contribute to this cracking, and without predicating the present disclosure on the validity of the theory, I offer as a suggestion the following possible explanations: The temperature change which occurs in each heat during furnace operation is probably one of the causes of failure. The structural changes produced at the hot face by accretions of iron oxide which built up on the brick from the open hearth furnace charge are also believed to be a factor. The migration of silicate which occurs from the hot face toward the region of crack formation furthermore contributes to failure.

In order to minimize the effects of temperature changes, the furnace operation must be adjusted to minimize temperature changes, but these changes can very rarely be eliminated, especially in an open hearth furnace using cold charge materials. Accordingly, it is very important to develop in the refractory a tolerance for temperature changes.

In order to overcome the effects of the accretions of iron oxide, I have produced a brick of increased resistance to iron oxide bursting by making up the brick from a mixture of coarser particles of chrome ore and finer par-

ticles of magnesia, the finer particles being free of chrome ore and the mixture being free of intermediate size particles as shown in my Patent No. 2,087,107 above referred to.

To minimize the effect of silicate migration, I choose raw materials for the brick which include a minimum of silica and also in some cases employ a ratio of lime to silica in the brick to minimize the formation of monticellite, which has a tendency to migrate. However, control of the chemical analysis of the brick is not too successful because, during the operation of the open hearth furnace, droplets of the slag are projected against the refractory during the boiling period in open hearth operation. Despite the fact that the furnace is a basic slag furnace, the boiling occurs while the slag is still in the formative stage and the material deposited on the refractory is likely to be relatively acid. I find that the slag pick-up on the brick has a lime-silica ratio of about unity. This slag, when absorbed by the brick, causes extensive silicate accumulation in a zone about 1" to 2" away from the hot face.

A brick which has been in service in a basic open hearth furnace may show the following type of slag migration and pickup. The percentages are by weight.

Zone	MM Behind Hot Face	SiO_2 percent	CaO percent
A	0-30	7.9	4.2
B	31-60	10.5	4.7
C	61-80	7.7	3.7
D	[1] 81-135	5.5	2.6

[1] Unaltered brick.

It will thus be evident that efforts to overcome the effects of silicate migration by use of carefully selected raw materials met with limited success. Furthermore, such selected raw materials are expensive and in an individual case may be difficult to obtain.

I have discovered that the resistance of a basic refractory brick to crack formation about an inch or two from the hot face can be increased by employing an internal structure on the refractory which is less susceptible to the effects of slag migration. It is thus possible to use ordinary chrome ore and dead burned magnesia and get much better resistance to silicate slag pickup. This advantage is particularly fruitful when unfired basic refractory is employed and especially where comolded steel plates are used, either internally or externally or in both positions.

To illustrate the improved result I will first describe the behaviour of a basic refractory brick of the type made under my U.S. Patent No. 2,087,107 above referred to. In a typical case, the refractory might be made from a mixture of 70 parts by weight of Philippine chrome ore in coarse particles passing through a 6 mesh per linear inch screen and resting on a 20 mesh per linear inch screen, 30 parts by weight of dead burned Austrian magnesite in fine particles through a 48 mesh per linear inch screen, one part by weight of kaolin, 1.1 parts by weight of sulfuric acid, and 2.7 parts by weight of water. The mixture is formed under a pressure of about 15,000 p.s.i. Such a brick, after treatment with carbon dioxide in accordance with my U.S. Patent No. 2,547,323, granted April 3, 1951, for Unburned Refractory Brick Making, and drying at 110° C. will typically have a modulus of rupture of 2000 p.s.i. and a Young's modulus of 8.0×10^6 p.s.i.

In order to determine the behaviour of such a brick when used in a furnace roof or wall where thermal gradients prevail, these brick have been placed in a panel using 9 x 4½ x 3 inch brick laid as headers. The panel has been heated in a preheating furnace of the character described in A.S.T.M. Spalling Test C38–49, heating for 24 hours at 1650° C. as described in A.S.T.M. C122–47 and C38–49.

After heating is finished, the furnace is cooled by shutting off the fuel and allowing the brick to cool in place. The cool panel is then taken apart and the individual brick removed. The test brick is sawed into 4½ x 3 inch pieces by passing a saw perpendicularly across the longitudinal axis of the brick at five stages spaced respectively 1" from one another and 1" from the hot face of the brick. This cutting operation is repeated with additional brick, but the saw is placed so that five pieces are obtained similar to the first series, excepting that the first cut produces a piece of one-half thickness at the hot face which is rejected and the next five saw stages are placed one inch from each other.

In this manner 10 pieces are obtained, each 4½ x 3 x ⅞ inch (allowing ⅛" thickness for the saw) and the average distance of each piece from the hot face increases serially from ½" to 5" in increments of approximately ½" as shown on the curves.

The Young's modulus (E) of each of these segments was determined using the conventional sonic method.

In FIGURE 1, curve A, I show the results obtained by plotting the values of Young's modulus (to be multiplied by 10^6) as ordinate against the average distance from the hot face as abscissa. The total percentage by weight of coarse particles was about 70 percent and the percentage of fine particles through 48 mesh per linear inch was about 30 percent. The coarse particles were 100 percent by weight chrome ore.

It is apparent from curve A that the application of heat to the unburned brick has caused alteration in the chemical bond originally formed by the sulfuric acid, carbon dioxide and moisture. The brick in the cooler zone, about 4½" from the hot face shows a Young's modulus of about 0.54×10^6 p.s.i. which is satisfactory. The brick at the extreme hot face shows a similar low Young's modulus, but in between in the range 2.0 there is a great rise in the values of E just behind the hot face to almost 6×10^6 p.s.i.

I have discovered that it is possible to minimize the increase in Young's modulus in the zone of 1" to 2" from the hot face independently of the silica content of the brick. This result is obtained not by minimizing the silica content in the segregated zone but by choosing a structure in the brick which offsets the bad effects of silicate migration.

Instead of using coarse chrome particles which pass through a 6 mesh per linear inch screen as in the case of brick of curve A, I employ chrome ore particles which are too large to pass through a 6 mesh opening, for example particles of 3.3 millimeters in diameter. These particles should desirably be as uniform as possible in size, for example small enough to pass a 4 mesh per linear inch opening or smaller than approximately 4.7 millimeters. By using chrome ore particles larger than 3.3 millimeters and smaller than 4.7 millimeters as opposed to chrome ore particles smaller than 6 mesh per linear inch (3.3 millimeters) and graded in size down to as small as 20 mesh per linear inch (0.8 millimeter), the distribution of pore space in the brick into which the silicates can migrate is more favorable and a small rise in Young's modulus at the segregated zone results.

The best values of Young's modulus can be obtained by using a mixture having coarse magnesia particles desirably smaller than 4 mesh per linear inch (4.7 millimeters) and larger than 6 mesh per linear inch (3.3 millimeters) (or 8 mesh per linear inch) with the coarse chrome particles. Increasing the amount of magnesia decreases the maximum Young's modulus as shown in FIGURE 1 by curve B and in FIGURE 2 by curve C and curve D. In the refractory brick submitted to the test described and used as a basis for plotting curves B, C and D the coarse particles constitute 70% by weight. In curve B the chrome coarse particles constitute 71% by weight of all the coarse particles, while in curve C the chrome coarse particles constitute 57% by weight of all

the coarse particles and in curve D the chrome coarse particles constitute 43% by weight of all the coarse particles, the balance of the coarse particles being magnesia.

It will be evident from examination of the Young's modulus on curves C and D that these brick show a much better resistance to crack formation when subjected to temperature changes than the brick shown in curve A.

It is not desirable to employ substantially less than 10 percent of the coarse particles as chrome ore coarse particles, as these stabilize the brick. In general the chrome coarse particles should constitute from 10 to 50 percent by weight of the refractory in the mix or preferably 10 to 40 percent.

The magnesia coarser particles may be the same size as the chrome coarser particles or if desired slightly smaller. In FIGURE 3 curve E, the magnesia coarser particles are substantially all too large to pass through a 20 mesh per linear inch screen (larger than about 0.8 millimeter) and in curve F the magnesia coarser particles are substantially all too large to pass through a 10 mesh linear inch screen (larger than about 1.6 millimeters). In both cases the brick contain 57 percent of the coarser particles as chrome particles through 4 mesh and on 6 mesh per linear inch. The total amount of coarser particles used in these brick was 70 percent by weight and the smaller particles were magnesia particles through 48 mesh per linear inch.

The problem of preparing the sized particles commercially will influence the choice of particle sizes. One difficulty encountered in choosing the desired chrome particles is that the fine particles which are formed by crushing and grinding the lump chrome ore cannot be used in the brick according to the present invention. Fortunately, chrome-magnesia brick may be made for installations where spall resistance is not an important factor and such brick generally employ chrome ore ground to pass a 6 mesh screen, so that the smaller size of chrome ore can be utilized. In the grinding and screening process for producing particles less than 6 mesh a large amount of the material is rejected because it is too large to pass a 6 mesh per linear inch screen and this material in prior practice must be reground. In the present invention this formerly rejected material is used and I find that a substantial part of it will pass a 4 mesh per linear inch screen. Thus chrome ore particles less than 4.7 millimeters and larger than 3.3 millimeters are obtained as a by-product in the manufacture of other brick and this is done without additional grinding and without producing fine particles which cannot be used.

In selecting magnesite particles the fine particles can all be used in the brick of the present invention. But there may be a scarcity of coarser magnesia particles as large as desired. In preparing some forms of magnesia such as those made from magnesium hydrate prepared from brine or sea-water, the supply of particles larger than 3.3 millimeters is limited. I therefore find it desirable to use smaller size magnesia particles, for example those passing through a 5 mesh per linear inch screen and too large to pass a 10 mesh per linear inch screen (between about 4.0 millimeters and 1.6 millimeters) or particles passing a 6 mesh per linear inch screen and too large to pass a 20 mesh per linear inch screen (between about 3.3 millimeters and 0.8 millimeter) as the coarse particles of magnesia.

In making up the brick the desired coarse chrome ore and magnesia particles and the fine magnesia particles are separated usually on inclined vibrating screens.

The coarser particles are of a size so that more than 90 percent of the coarser particles by weight rest on a 28 mesh screen, more than 80 percent of the coarser particles by weight rest on a 14 mesh screen and more than 35 percent rest on an 8 mesh screen, or preferably a 6 mesh screen.

In making up the mix, 10 to 50 percent (preferably 10 to 40 percent) by weight of the refractory material is

coarser chrome ore particles, which meet the above size requirements for coarser particles. These chrome ore particles are preferably smaller than 4 mesh.

The balance of the coarser particles in the preferred embodiment will constitute the magnesia coarser particles which also follow the size range suggested above for coarser particles and are also preferably smaller than 4 mesh.

It may be desirable in certain cases to use coarser particles all of which are larger than 10 mesh or even all larger than 6 mesh but desirably below 4 mesh.

In the preferred embodiment 80 percent by weight of the coarser particles are substantially all larger than 10 mesh and in the most desirable form more than 80 percent by weight of the coarser particles are substantially all larger than 6 mesh.

The refractory mixture will contain 10 to 35 percent of fine magnesia particles substantially all of which are finer than 48 mesh (0.3 millimeters) based on the total weight of refractory particles.

In preparing particles too large to pass the openings of a standard 6 mesh or 8 mesh screen, it must be kept in mind that commercial screening is not perfect to the point where 100 percent of such particles will rest on a 6 or 8 mesh screen in the standard screen test. I can use coarse particles having 10 percent or even as much as 20 percent passing through the 6 mesh or 8 mesh standard screen.

By this method of using separately prepared coarse particles and/or separately prepared fine particles the mixture is unnaturally low in intermediate size particles between 48 and 28 mesh per linear inch as such particles are not included. Of course a minor amount of intermediate particles will still be found in the mixture due to limits in efficiency of separation or other causes. However, the coarse particles should not exceed about 10 percent through 28 mesh and the intermediate size particles should not exceed 10 percent of the total weight of the brick.

In the brick of the invention as a bond I employ between 0.5 and 5 percent and preferably between 1 and 3 percent of the total weight of the dry refractory ingredients of sulphuric acid, or magnesium sulphate, or chromic acid, or hydrochloric acid, or magnesium chloride, or sodium chromate, or sodium dichromate, or sodium silicate, or sulfite paper waste (lignin waste), or carbohydrate (dextrin, starch, sugar), or pitch, tar or tall oil. These bonds become active after drying.

In producing the preferred bond, I add in a wet pan a solution of sulfuric acid sufficient to give 1.1 parts by weight of acid and 2.7 parts by weight of water to 65 to 90 parts by weight of coarse particles and 10 to 35 parts by weight of fine particles. This water is the amount of water needed for good pressing. In some cases I also introduce a mineral binder such as finely ground kaolin (about 1% by weight) and/or metallic iron powder passing 28 mesh and preferably passing 100% through 200 mesh (about 1 to 15% preferably 5% by weight).

The quantities of these binders are based on the total weight of refractory particles and are over and above the 100 percent of refractory particles. The mixture is pressed into brick form under pressure exceeding 5000 p.s.i., but permissibly 15,000 p.s.i. or more.

In many embodiments suitably formed steel sheets are introduced into the mold, either into the interior of the refractory mass or on the surface or in both places, so that the refractory will be comolded with the steel and the brick will have an external comolded casing of steel, preferably on its four lateral faces or parts thereof together with internal plates, preferably two or more extending longitudinally through the brick. These steel plates serve to reduce spalling of the brick and serve to reenforce the brick during shipment and service and therefore offset any disadvantages that may rise due to presence of unnaturally large particles in the brick. These reenforcing is particularly helpful in protecting the corners

and edges of the brick containing such unusually coarse particles.

In the preferred embodiment the brick, after molding, are treated with carbon dioxide gas as disclosed in my U.S. Patent No. 2,547,323 and then dried at temperatures above 110° C. The brick are then ready for use.

The brick of the present invention are recommended for roofs of open hearth steel furnaces and other metallurgical furnaces, particularly suspended roofs, and suspended or normal wall construction such as open hearth front walls, back walls, ends, downtakes and the like.

All percentages and parts stated are by weight.

It will be evident that the composition of the invention will in some cases be used to make up the portion of the refractory brick which is employed adjacent the hot end, and a sufficient distance from the hot end to include the portion of the brick which is to be subjected to furnace temperature as the brick erodes away, while a different composition specially suitable for use near the cold end may be employed at the cold end. In other cases the brick will be composed entirely of the refractory according to the invention.

The screen sizes used here are the Tyler Standard Screen Scale Sieves as adopted by the United States Bureau of Standards.

In view of my invention and disclosure, variations and modifications to meet individual whim or particular need will doubtless become evident to others skilled in the art, to obtain all or part of the benefits of my invention without copying the composition, and I, therefore, claim all such insofar as they fall within the reasonable spirit and scope of my claims.

Having thus described my invention, what I claim as new and desire to secure by Letters Patent is:

1. A refractory brick, unfired and suitable for use without kiln firing, consisting essentially of refractory material made up of a mixture of coarser magnesia particles, coarser chrome ore particles and finer magnesia particles, unnaturally low in particles of intermediate size, the coarser particles being of a size so that more than 90 percent of the coarser particles by weight rest on a 28 mesh screen, more than 80 percent of the coarser particles by weight rest on a 14 mesh screen, and more than 35 percent of the coarser particles by weight rest on an 8 mesh screen, the coarser particles making up 65 to 90 percent by weight of the refractory material, 10 to 50 percent by weight of the refractory material being coarser chrome ore particles, the finer particles being smaller than 48 mesh, making up 10 to 35 percent by weight of the refractory material, and substantially free from chrome ore, and including as bond based on the weight of refractory material a bonding substance which is active after drying of the class consisting of from 0.5 to 5 percent of sulfuric acid, magnesium sulphate, chromic acid, hydrochloric acid, magnesium chloride, sodium chromate, sodium dichromate, sodium silicate, sulphite paper waste, carbohydrate, pitch, tar and tall oil.

2. A refractory brick of claim 1, in which the coarser particles are all smaller than 4 mesh.

3. A refractory brick of claim 1, in which the coarser chrome particles are substantially all smaller than 4 mesh.

4. A refractory brick of claim 1, in which the coarser particles, other than chrome particles, are substantially all magnesia particles smaller than 4 mesh.

5. A refractory brick of claim 1, containing 1 to 15 percent of iron powder passing 28 mesh, based on the total weight of refractory material.

References Cited in the file of this patent

UNITED STATES PATENTS

2,639,993	Heuer	May 26, 1953
2,656,280	Heuer	Oct. 20, 1953