

Feb. 19, 1963

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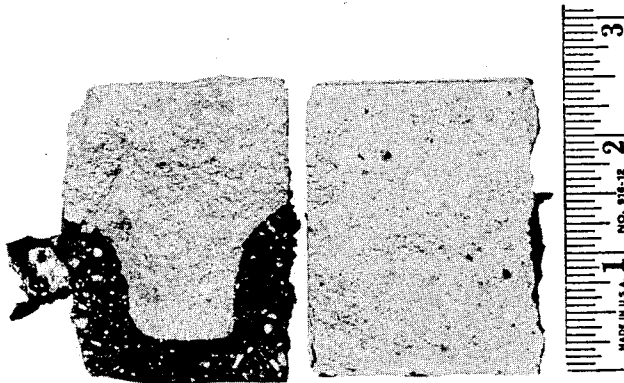
ALUMINUM MELTING FURNACE REFRACTORY

Filed Nov. 8, 1960

2 Sheets-Sheet 1

Fig. 1

Fig. 2



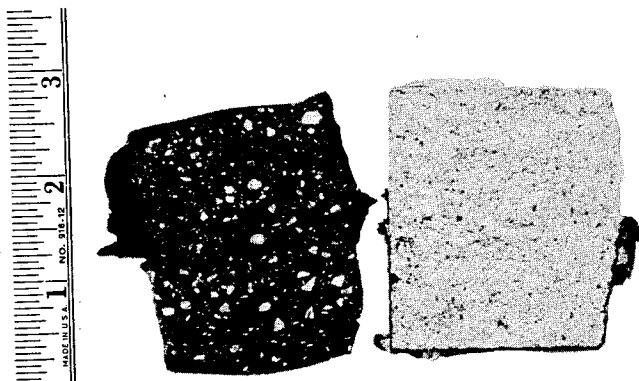
Composition A
Commercial Standard

Composition K
This invention

Each exposed 3 days in 70-75 aluminum alloy at 1500°F.

Fig. 3

Fig. 4



Composition A

Composition K

Each exposed 3 weeks in 70-75 aluminum alloy at 1500°F.

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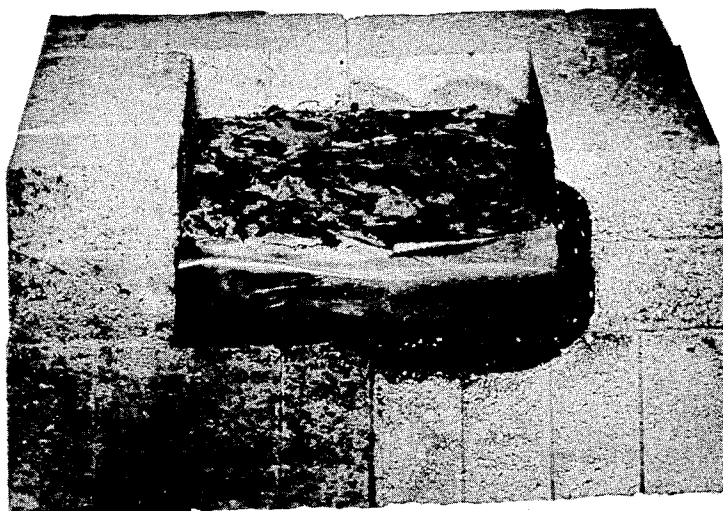
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ALUMINUM MELTING FURNACE REFRACTORY

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2 Sheets-Sheet 2

Fig. 5



Composition B

Composition A

This invention

Commercial standard

70-75 aluminum alloy held 3 days at 1500°F.

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ALUMINUM MELTING FURNACE REFRACTORY
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Filed Nov. 8, 1960, Ser. No. 67,955
8 Claims. (Cl. 106—62)

This invention relates to aluminum melting furnaces, and more particularly to essentially non-vitreous refractories for the construction of such furnaces.

In the aluminum industry furnaces are used for remelting aluminum or for holding it in the molten state upon receiving it from other melting furnaces or from the electrolytic cells in which it is produced. For brevity all such furnaces are referred to herein as melting furnaces. The molten aluminum in such furnaces may receive other metals, such as magnesium, manganese, zinc and copper, as alloying additions.

In secondary melting operations for the recovery of aluminum metal from scrap, fluxes or refining agents are commonly added to the molten aluminum. Thus, there may be additions of mixtures of chlorides, such as sodium and potassium chlorides, aluminum and zinc chlorides, and additions of cryolite, or chlorine gas may be bubbled through the metal.

The hearth and lower side walls which are in contact with the molten aluminum are subject not only to erosion but also to corrosive attack by the metal and by fluxes where they are used. Various types of refractory brick have been tried for aluminum melting furnaces but the problem of chemical attack has not been solved, particularly in the severest fluxing practice and in the melting of corrosive aluminum alloys. The attack on the refractory is especially severe at the metal line, where the level of the molten metal fluctuates during charging and tapping, and due to fluxes and the buildup of dross. This dross buildup, which reduces furnace capacity, is composed principally of aluminum and aluminum oxide. Although the dross can be removed with only moderate difficulty while it is still soft, it soon becomes very hard and so firmly attached to the refractory that its removal by mechanical means damages the refractories.

Another problem which must be considered is the fact that aluminum reacts with siliceous compounds, including silica, in the refractories with resultant contamination of the metal with silicon. Accordingly, when high purity metal is involved, refractories containing a substantial percentage of available silicon compounds cannot be tolerated.

For many years dense fire clay brick, such as those employed in blast furnaces, were found to be satisfactory and, even today, continue to give acceptable service when there is little or no use of alloying or fluxing additions and silicon pick-up is not objectionable. However, the demand for higher production rates, the present rigid alloy specifications, and the corrosiveness of fluxes and alloying additions have necessitated the development of new refractories to meet these requirements.

Aluminum melts at about 1220° F., tapping temperatures exceed 1300° F., and the metal temperature in the furnace ranges between 1300° and 1500° F. Temperatures of the furnace atmosphere are higher, of course, since these control the rate of working, and usually are 2000° F. or more. Thus the refractories for these purposes must possess an adequate degree of refractoriness.

The most common mechanism of refractory attack in furnaces of the type involved is marked by the penetration of the brick by the extremely fluid molten aluminum metal, accompanied by such reactions as oxidation of the absorbed aluminum and the reduction of silicates to silicon, with deposition of elemental silicon within the brick.

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These reactions frequently cause expansion of the refractory and an inward heaving of the wall, particularly at the metal line, as well as tending to cause spalling. Therefore the absorption of aluminum or aluminum alloys by the refractory is indeed objectionable. These brick must, moreover, be adequately strong and tough to withstand mechanical abuse from impact and abrasion caused by the charging of ingots and scrap.

It is among the objects of this invention to provide essentially non-vitrified refractories of improved resistance to penetration and attack by molten aluminum, which possess strength and related properties requisite to sustain the mechanical abuse just referred to, which are of simple composition, which may be made easily in accordance with normal refractory production practices from well known and readily available materials, and which are comparable in cost to the better grades of refractories now used in furnaces for holding molten aluminum.

A further object is to provide furnaces for melting aluminum and for holding molten aluminum which exhibit minimized attack by liquid aluminum and its alloys in comparison with such furnaces presently in use.

Yet another object is to provide a method to minimize attack of high alumina refractories by molten aluminum which is simple, economical, readily practiced and effectively minimizes deterioration of the refractories in use.

Other objects will appear from the following specification.

The invention will be described in connection with the accompanying photographs in which:

FIG. 1 is a view of a portion of a brick, which has been the commercial standard for aluminum melting, after it had been exposed to molten aluminum alloy;

FIG. 2 is a similar view of a portion of a brick according to this invention after exposure the same as FIG. 1;

FIG. 3 is a view of brick of FIG. 1 after longer exposure;

FIG. 4 is a view of brick of FIG. 2 after exposure the same as FIG. 3; and

FIG. 5 is a view of a section through a hearth in which molten aluminum has been held and of which the right hand half was constructed of the brick of FIGS. 1 and 3, and the left hand half of brick in accordance with this invention.

High alumina refractory brick have been widely used for the construction of aluminum melting furnaces, because of their good physical properties and because their low silica content results in a minimum of silicon contamination of the metal. However, all of the brick of this type known heretofore have been subject, as far as I am aware, to penetration and chemical attack after a relatively short period of use. There has, as a result, been a demand not only for a refractory possessing the physical qualities of the high alumina type but also possessing greatly improved resistance to the objectionable action of molten aluminum and its alloys.

I have discovered, and it is upon this that the invention is primarily predicated, that the objects of the invention are attained with refractory compositions which contain, by weight, at least 50 percent of Al_2O_3 , by analysis, supplied by refractory material of the group alumina and high alumina ores, and which contain also a small percentage of at least one alkaline earth oxide, by analysis. The alkaline earth oxide may be present in an amount from about 1 to 30 percent by weight, preferably about 2 to 8 percent, and it acts in some manner that is not wholly explicable to greatly increase the resistance of the refractory to penetration of and attack by molten aluminum and alloying additions. Instead of alkaline earth oxide there may be used alkaline earth compounds, such as the carbonates (e.g. dolomite or magnesite), that provide the stated amount of oxide. The term "by analysis" as used

herein means that upon analysis the stated amount will be found to be present even though combined with or in admixture with other substances.

For refractories of very high Al_2O_3 content alumina will, of course, be used, suitably in the form known as tabular alumina. Where such high Al_2O_3 content is not needed the Al_2O_3 may be provided by bauxites or other aluminum ores of high Al_2O_3 content (about 50 percent or more). Of course, such ores may be blended with alumina to supply an increased content of Al_2O_3 .

Thus the refractory will comprise alumina and the alkaline earth oxide together with constituents normal to the materials supplying them. The compositions should be such that any glassy phase in the fired product is, if present, in very low amount, i.e., the burned product is essentially non-vitrified for any glassy phase is present in but an insignificant amount. Also, because they exert a fluxing action that can seriously impair the properties of these refractories, especially their resistance to attack by aluminum, alkali metal compounds should as far as possible be avoided but in any event should be present in an amount less than 5 percent by weight of the refractory.

Alumina possesses little plasticity so that in the forming of shaped refractories it is generally necessary to have present a plasticizing agent in order that the refractory shapes can be handled subsequent to forming. For many purposes ball clay is suitable but because of its silicate nature it should be present in minor amount, say not in excess of 15 percent, preferably not over 10 percent. Other non-mineral plasticizers can be used instead of clay, a variety of which are known and used in the refractory trade, examples being lignin liquor, molasses, and carboxymethylcellulose. Such organic adjuvants are burned out when the refractory is fired, or when the refractory is put in use in the case of chemically bonded and unfired shapes.

As will appear, other refractory materials, such as mag-

The refractories provided by this invention may be made by normal methods of refractory manufacture. Thus the raw materials may be crushed to a brick-making grind which will give a brick of high density, low porosity, and good thermal shock resistance. Such grinds are quite standard and they are well understood in the refractory trade. To obtain such properties the grind should be such as to provide a batch of particles graded from coarse to fine, but at least 50 percent should be coarser than 150-mesh (Tyler) because grinds containing much more than 50 percent by weight finer than 150 mesh cannot be satisfactorily pressed into brick by standard brick-making practices. An example of such a grind suited to the purpose of this invention is, by weight:

	Percent
-6 +10 mesh (Tyler)-----	15
-10 +28-----	25
-28 +65-----	17
-65-----	43

The appropriate grind is thoroughly mixed in standard equipment and sufficient liquid, such as water or lignin liquor, is added to temper the batch, which is then pressed or otherwise formed into brick under high pressure. In usual practice the brick are then air dried followed by oven drying. In the case of chemically bonded brick, which are well understood in the trade, the shapes are then ready for installation. Where fired brick are to be produced the dried brick are then fired at a temperature to produce the desired physical properties but below a temperature that will cause vitrification.

The brick provided by the invention are useful for the construction of the hearths and side walls of aluminum melting furnaces, as will be clear from the tests reported hereinafter.

The following tables are exemplary of the practice of the invention and the benefits to be derived from it:

Table I

[Compositions in weight percent]

	A	B	B-1	C	D	D-1	E	F	F-1	H	J	K	L
Tabular Alumina-----	85	81	77	81	81	77	81	81	77	81	10	---	---
Ball Clay-----	15	15	15	15	15	15	15	15	15	15	2	2	2
Sinter A-----	---	4	8	---	---	---	---	---	---	---	---	---	---
CaO (added as $\text{Ca}(\text{OH})_2$ -----	---	---	---	4	---	---	---	---	---	---	---	---	---
CaO (added as CaCO_3)-----	---	---	---	---	4	8	---	---	---	---	---	---	---
CaO+MgO (added as Dolomite)-----	---	---	---	---	---	---	4	---	---	---	---	---	---
BaO (added as BaCO_3)-----	---	---	---	---	---	---	---	4	8	---	---	---	---
B_2O_3 (added as H_3BO_3)-----	---	---	---	---	---	---	---	---	---	4	---	---	---
So. Amer. Bauxite (calcined)-----	---	---	---	---	---	---	---	---	---	---	70	90	70
Nevada Magnesite (dead burned)-----	---	---	---	---	---	---	---	---	---	---	18	8	28

Table II

[The analysis of the materials was as follows]

Tabular Alumina	Ball Clay	Sinter A	Dolomite	Calcined South American Bauxite	Nevada Magnesite
99.4% Al_2O_3 . 0.3% SiO_2 . 0.2% Fe_2O_3 . 0.1% Alkaline Earth Oxides.	30.3% Al_2O_3 . 53.6% SiO_2 . 1.7% TiO_2 . 0.9% Fe_2O_3 . 0.49% $\text{CaO} + \text{MgO}$. .41% $\text{Na}_2\text{O} + \text{K}_2\text{O} + \text{Li}_2\text{O}$. 12.4% Ignition Loss.	46.0% B_2O_3 . 23.8% BaO . 17.7% SiO_2 . 7.1% Al_2O_3 . 4.9% CaO . 0.5% $\text{MgO} + \text{Alkalies}$. 0.2% Fe_2O_3 . 0.1% TiO_2 .	54.0% CaO . 37.5% MgO . 7.25% $\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3$. 0.91% SiO_2 . .34% Ignition Loss.	88.58% Al_2O_3 . 6.21% SiO_2 . 3.37% TiO_2 . 1.56% Fe_2O_3 .	85.7% MgO . 5.09% CaO . 4.34% SiO_2 . 4.05% Fe_2O_3 . 0.79% Al_2O_3 .

nesite (an alkaline earth oxide) may be present in substantial amounts in these refractories with, commonly, a plasticizer of clay or bentonite or of organic type. In either instance the refractory will, in use, consist essentially of alumina, alkaline earth oxide and refractory material other than alumina, apart from oxides present in minor amounts, usually as impurities in the base materials. Commonly such other oxides will be silica, titania, and iron oxide. Such other refractory material should be of low silica content.

In each example, the ingredients were crushed to the foregoing grind and thoroughly mixed dry. About 3 to 6 percent by weight of water was added and the batches were then pressed into 9 x 4½ x 2½" straights at about 4000 p.s.i. The shapes were air dried for about 24 hours and then oven dried at about 230° F. overnight. Following this they were fired for 10 hours at about 2550° F. The effect of molten aluminum was determined by immersing specimens of the bricks about 2 x 2 x 2½ inches to about one-half their height in molten aluminum alloy

for 72 hours at 1500° F. In this test there was used molten aluminum alloy 7075 which contains 5.5% of zinc, 2.5% of magnesium and 1.5% of copper. This alloy has been observed to attack the standard high alumina brick very severely. The specimens were then removed from the bath and cut in half to observe the penetration caused by the metal. This test simulates attack at the metal line where the attack is most severe. The results of this test and others when applied to the foregoing compositions are given in the following Table III.

Table III

	A	B	B-1	C	D	D-1	E
Weight, p.c.f.	171	170	167	162	162	156	166
Modulus of Rupture, p.s.i.	1,050	2,630	3,300	1,370	1,380	950	1,890
Apparent Porosity, percent	21.5	19.1	17.8	25.2	25.2	28.1	23.1
Linear Change in Burning, percent	+0.3	+0.2	+0.3	0.0	0.0	0.0	+0.3
Aluminum Immersion Test, Penetration Range, Inches	1/8 to 1	10 to 3/16	10 to 1/8	0	10 to 3/16	0	10 to 1/8
Prevailing Penetration	1" Max.	0	0	0	0	0	0

	F	F-1	H	J	K	L
Weight, p.c.f.	172	168	154	160	165	146
Modulus of Rupture, p.s.i.	1,280	920	1,540	1,280	870	290
Apparent Porosity, percent	20.7	20.7	23.4	28.4	24.7	33.6
Linear Change in Burning, percent	+0.2	+0.5	+0.7	+3.4	+1.7	+5.0
Aluminum Immersion Test, Penetration Range, Inches	0	0	3/4-3/8	0	0	0
Prevailing Penetration	0	0	3/4	0	0	0

1 Spot penetration.

It will be observed from Table III of test results that all of the bricks except H showed in comparison with the base A brick a great improvement in resistance to penetration by the alloy. Base mix A, which contained no alkaline earth addition, is a commercial brick heretofore considered to be the best for melting aluminum. Examples B and B-1 were supplied with alkaline earth oxide in the form of sinter A, which as shown above contained in addition to 28.7% of CaO and BaO a substantial proportion of boric oxide. This led to investigating the effect of boric oxide in the form of Example H but, as appears from the table, it was severely attacked. It may be noted also that much dross adhered to Examples A and H, a little dross adhered to Examples B and B-1 while no dross adhered to the remaining specimens.

Visual proof of the important character of the present invention is given by the appended photographs which represent the results of tests made in the manner and with the alloy described above. FIG. 1 was a brick of composition A, Table I. FIG. 2 shows the brick of composition K, representative of the present invention. These specimens were immersed to a depth of 1 1/2 inches for three days in the 7075 alloy at 1500° F. Two things are immediately evident upon examining these photographs, namely, the extensive penetration of the composition A refractory, FIG. 1, with deposition of elemental silicon and extensive dross accumulation on the sides of the specimen whereas in contrast the composition K refractory, FIG. 2, showed no penetration whatsoever and only a slight accumulation of dross on one face. FIGS. 3 and 4 show what had occurred after three weeks immersion in the same alloy at the same temperature. By this time the commercial standard brick of composition A (FIG. 3) had been completely penetrated and completely filled with elemental silicon and with extensive dross accumulation. Yet composition K (FIG. 4) after the same exposure showed only an extremely narrow band of penetration and insignificant dross accumulation.

FIG. 5 is a section through a pilot hearth melting furnace the right half of which was constructed from the commercial standard composition A while the left half of which was constructed from mix B of Table I. This was heated to 1500° F. and 7075 alloy was placed

on it and the temperature was maintained for three days. After cooling the hearth was sectioned vertically as shown in the photograph. Here again the extensive penetration of mix A with silicon is evident while in striking contrast the bricks of mix B have not been penetrated. Examination of the photograph indicates slight dross accumulation on the mix B bricks of this invention in contrast to appreciable accumulation on mix A bricks.

Shapes, such as bricks, may be made in various ways other than described above. For example, they may be

made by mixing finely divided alkaline earth oxide and finely divided high alumina material, e.g. bauxite, tempering the mixture to an extruding consistency with water, extruding the mixture, drying and firing the extruded "dobie" to about 2500° to 2700° F., thereby producing a very dense "dobie." The resultant product is then crushed to a standard brick-making grind, such as that given above, and brick are made from it using standard techniques. In this manner the alkaline earth oxide is incorporated in each grain of the brick.

As evidencing the use of larger amounts of alkaline earth oxide than are represented by the compositions of Table I, reference may be made to one test involving, by weight, 70.4 percent of crude Alabama bauxite and 29.6 percent of barium carbonate. Grog and "dobies" were made from this mixture as described in the immediately preceding paragraph and the "dobies" were burned in the same way for five hours. The "dobies" were then ground and brick were made from the following mix:

	Percent
Grog from "dobies"-----	79.4
Crude South American bauxite-----	12.1
Ball clay-----	3.5
Barium carbonate-----	5.0

The brick were pressed and fired in the manner described in connection with Table I. As fired they weighed 156 pounds per cubic foot, their modulus of rupture was 900 p.s.i., their apparent porosity was 27 percent, and their linear change in burning was minus 1.1 percent.

These fired brick were then subjected to the aluminum immersion test described above in connection with the bricks of Table I. They showed zero penetration by aluminum, both prevailing and as to range. There was no dross build-up on them, and they showed only the faintest trace of reaction between the aluminum alloy and the refractory.

The calculated chemical analysis of these latter brick is:

	Percent
Alumina -----	51.7
Silica -----	14.7
Barium oxide-----	30.9
Remainder -----	2.7

The chemical analysis of the Alabama bauxite used in this test was, on the calcined basis:

	Percent
SiO ₂ -----	21.3
Al ₂ O ₃ -----	75.0
TiO ₂ -----	2.6
Fe ₂ O ₃ -----	1.1
CaO -----	0.1
Ign. loss -----	0.1

Although the invention has been described with particular reference to the production of shaped refractories, it may be applied in the form of refractory monoliths. Also, the refractories may contain other refractory materials in minor amounts that do not deleteriously affect the properties characteristic of the invention, such, for example, as zircon, chrome ore, zirconia, silicon carbide, and the like, due regard being had to the limitations set down above on alkali metal compounds, silica, and glasses phase.

This application is a continuation in part of my copending application Ser. No. 822,190, filed June 23, 1959, now abandoned.

In accordance with the provisions of the patent statutes, I have explained the principle of my invention and have described what I now consider to represent its embodiment. However, I desire to have it understood that, within the scope of the appended claims, the invention may be practiced otherwise than as specifically described.

I claim:

1. A fired refractory brick, said brick characterized by resistance to penetration and reaction with molten aluminum and its alloys, and consisting essentially of, by weight, from about 1 to 30% of a substance of the group consisting of alkaline earth oxides and alkaline earth compounds supplying that amount of alkaline earth oxide, the remainder substantially all material of the group consisting of alumina and aluminum ores containing, by oxide analysis, at least about 50% of Al₂O₃, said substance and said material being present in a brickmaking graded size range, at least about 50% thereof being coarser than 150 mesh, said brick being characterized as substantially free of any glassy phase and having less than about 30% apparent porosity.

2. That method of making refractory brick characterized by resistance to penetration by and reaction with molten aluminum and its alloys, comprising providing a batch of size graded refractory material at least about 50%, by weight, of which is coarser than 150 mesh, said material consisting essentially of, by weight, about 1 to 30% of a substance of the group consisting of alkaline earth oxide and alkaline earth compounds supplying that

amount of alkaline earth oxide, the remainder of the batch being substantially all material of the group consisting of alumina and aluminum ores containing at least about 50% Al₂O₃, by weight and on the basis of an oxide analysis, tempering said batch, shaping the tempered batch to provide shapes having low porosity, drying the shapes, firing the shapes to a temperature below which any substantial glassy phase is produced.

3. A fired refractory brick, said brick characterized by resistance to penetration and reaction with molten aluminum and its alloys and consisting essentially of, by weight, about 1 to 30% of a substance of the group consisting of alkaline earth oxides and alkaline earth compounds supplying that amount of alkaline earth oxide, the remainder being substantially all high alumina bauxite, said substance and said bauxite present in a brickmaking graded size range, at least about 50% thereof being coarser than 150 mesh, said brick being characterized as substantially free of any glassy phase, and said brick having less than about 30% apparent porosity.

4. A fired refractory brick, said brick characterized by resistance to penetration and reaction with molten aluminum and its alloys and consisting essentially of, by weight, about 1 to 30% of a substance of the group consisting of alkaline earth oxides and alkaline earth compounds supplying that amount of alkaline earth oxide, about 70 to 85% of alumina, and the remainder substantially all ball clay, said substance, alumina, and ball clay being present in a brickmaking graded size range, at least about 50% of which is coarser than 150 mesh, and brick being characterized as substantially free of any glassy phase, and said brick having less than about 30% apparent porosity.

5. The brick of claim 4 in which the substance is dead burned magnesite.

6. Brick according to claim 1 containing not over about 5 percent by weight of alkali metal oxides by analysis.

7. A method according to claim 2, the batch containing not over about 5 percent by weight of alkali metal oxides by analysis.

8. Brick according to claim 4 containing not over about 5 percent by weight of alkali metal oxides by analysis.

References Cited in the file of this patent

UNITED STATES PATENTS

2,308,115	Schwartzwalder et al.	Jan. 12, 1943
2,310,953	Heany	Feb. 16, 1943
2,760,875	Schwartzwalder et al.	Aug. 28, 1956

FOREIGN PATENTS

487,957	Great Britain	June 29, 1938
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