

(CONVENTION. By one or more persons and/or a Company.)

Form 4

616704

COMMONWEALTH OF AUSTRALIA

Patents Act 1952-1969

CONVENTION APPLICATION FOR A PATENT

(1) Here
insert (in
full) Name
or Names of
Applicant or
Applicants,
followed by
Address (es).

XXX(1) ALCAN INTERNATIONAL LIMITED
We
of 1188 Sherbrooke Street W., Montreal, Quebec,
Canada

(2) Here
insert Title
of Invention.

hereby apply for the grant of a Patent for an invention entitled: (2)
REFRACTORY MATERIAL PRODUCED FROM RED MUD

(3) Here insert
number(s)
of basic
application(s)

which is described in the accompanying complete specification. This application is a
Convention application and is based on the application numbered (3)

552,914

(4) Here insert
Name of basic
Country or
Countries, and
basic date or
dates

for a patent or similar protection made in (4) Canada
on 26th November 1987

My address for service is Messrs. Edwd. Waters & Sons, Patent Attorneys,
25/1 Our 50 Queen Street, Melbourne, Victoria, Australia.

DATED this 24th day of November 19 88

(5) Signa-
ture (s) of
Applicant (s)
or
Seal of
Company and
Signatures of
its Officers as
prescribed by
its Articles of
Association.

(5)

ALCAN INTERNATIONAL LIMITED

by

Stephen K. Plymin

Registered Patent Attorney

(CONVENTION. Company.)

Form 8

COMMONWEALTH OF AUSTRALIA

Patents Act 1952-1969

DECLARATION IN SUPPORT OF A CONVENTION
APPLICATION FOR A PATENT OR PATENT OF ADDITION(1) Here
insert (in
full) Name of
Company.In support of the Convention Application made by⁽¹⁾.....
ALCAN INTERNATIONAL LIMITED

(hereinafter referred to as the applicant) for a Patent

(2) Here
insert title
of Invention.for an invention entitled:⁽²⁾.....

REFRACTORY MATERIAL PRODUCED FROM RED MUD

(3) Here
insert full Name
and Address,
of Company
official
authorized
to make
declaration.I, ⁽³⁾..... PAUL J. LEMIEUX
of 1188 Sherbrooke Street W., Montreal, Quebec, Canada

do solemnly and sincerely declare as follows:

1. I am authorised by the applicant for the patent
to make this declaration on its behalf.2. The basic application as defined by Section 141 of the Act was
made in⁽⁴⁾..... Canada
on the 26th day of November 1987, by CLAUDE ALLAIRE
on the ~~xxxx~~ day of ~~xxxx~~ 19~~xxxx~~(4) Here
insert basic
Country or
Countries
followed by
date or dates
and basic
Applicant or
Applicants.3. ⁽⁵⁾..... CLAUDE ALLAIRE,
of 207 Colbert, Chicoutimi-Nord,
Quebec, Canada G7G 1L6(5) Here
insert (in
full) Name
and Address
of Actual
Inventor or
Inventors.I ~~am~~ are the actual inventor of the invention and the facts upon which the applicant
is entitled to make the application are as follow:The applicant is the assignee of Claude Allaire by virtue of
an assignment dated December 8, 19874. The basic application referred to in paragraph 2 of this Declaration
was.....the first application made in a Convention country in
respect of the invention the subject of the application.DECLARED at Kingston, Ontario
this 11th day of November 1988
ALCAN INTERNATIONAL LIMITED

(6) Signature.

(6) by

Paul J. Lemieux,
Patent Manager

To: THE COMMISSIONER OF PATENTS.

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(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 616704

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REFRACTORY MATERIAL PRODUCED FROM RED MUD
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WATERMARK PATENT & TRADEMARK ATTORNEYS , Locked Bag 5, HAWTHORN VIC 3122
- (56) Prior Art Documents
US 3985567
US 3879211
AU 457435 31428/71 B28C 3/00
- (57) Claim

1. A process for producing a refractory material which is resistant to corrosion by alkaline materials and fluorides at high temperature, which process comprises: calcining red mud containing Bayer sodalite at a temperature in the range of about 900 to 1400°C for a time sufficient to remove combined water and to produce nepheline from said Bayer sodalite in said red mud; grinding the product following calcination to the -4 Tyler mesh range; mixing the ground product with a binder, other than a clay, suitable for producing stable cryolite-resistant mineral phases in said refractory material, said binder being selected from the group consisting of silica-containing particulate materials or precursors thereof, alumina-containing particulate materials or precursors thereof, and mixtures thereof, in an amount sufficient to bind the ground product upon firing, and sufficient water to produce a formable mixture, wherein the amount of ground product and binder is such that the ratio of red mud to other ingredients is sufficient to provide a fired refractory material product which comprises at least 90% by weight of red mud, and wherein the alumina content of the ground product and binder is increased by addition, if

(11) AU-B-25917/88
(10) 616704

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necessary, so that it amounts to at least 10% more than that which becomes combined in nepheline formed in the refractory material; forming the mixture into a shaped product; and firing the shaped product at a temperature in the range of about 900 to 1400°C to produce said refractory material.

18. An aluminum electrolysis cell comprising a container having a refractory lining holding cell contents which include a molten sodium compound, said lining comprising a refractory material which is resistant to corrosion by alkaline materials and fluorides at high temperature produced by: calcining red mud containing Bayer sodalite at a temperature in the range of about 900 to 1400°C for a time sufficient to remove combined water and to produce nepheline from said Bayer sodalite in said red mud; grinding the product following calcination to the -4 Tyler mesh range; mixing the ground product with a binder, other than a clay, suitable for producing stable cryolite-resistant mineral phases in said refractory material, said binder being selected from the group consisting of silica-containing particulate materials or precursors thereof, alumina-containing particulate materials or precursors thereof, and mixtures thereof, in an amount sufficient to bind the ground product upon firing, and sufficient water to produce a formable mixture; forming the mixture into a shaped product; and firing the shaped product at a temperature in the range of about 900 to 1400°C to produce said refractory material.

COMMONWEALTH OF AUSTRALIA

Form 10

PATENTS ACT 1952-69

COMPLETE SPECIFICATION

(ORIGINAL)

616704

Class

Int. Class

Application Number:
Lodged:

Complete Specification Lodged:

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Related Art:

Name of Applicant: ALCAN INTERNATIONAL LIMITED

Address of Applicant: 1188 Sherbrooke Street W., Montreal, Quebec, Canada

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50 QUEEN STREET, MELBOURNE, AUSTRALIA, 3000.

Complete Specification for the invention entitled:

REFRACTORY MATERIAL PRODUCED FROM RED MUD

US

The following statement is a full description of this invention, including the best method of performing it known to:

Refractory material produced from red mud

This invention relates to refractory materials and to a process for producing such materials from red mud. More particularly, the invention relates to such refractory materials which are suitable for use as cell linings in aluminum production cells.

Red mud is a by-product of alumina production processes and it is often discarded as waste, but this is economically and environmentally disadvantageous. Many attempts have been made over the years to find a use for red mud but none has proved to be particularly satisfactory. For example, since red mud contains a large proportion of iron oxide, attempts have been made to smelt the mud for the recovery of iron but without commercial success.

British patent 1,491,432 published on November 9, 1977 in the name of Chemokomplex Vegyipari Gép-És Berendezés Export-Import Vállalat et al, discloses the use of red mud for the production of shaped ceramic products. This is achieved by mixing the red mud with silica, silicates or similar materials, or dolomite to the extent of 10-49% by weight (on a dry weight basis), shaping the resulting mixture and then firing it at 950-1250°C. However, the resulting materials are not satisfactory for applications involving alkaline and fluorine corrosion at high temperature, such as cell linings for aluminum production cells where cryolite components, mainly NaF, are involved. Moreover, the products have a tendency to shrink during firing and thus may crack.

~~It is therefore an object of the present invention to utilize red muds to form high temperature and cryolite-resistant refractories suitable for use as linings in aluminum production cells.~~

According to one aspect of the invention there is provided a process for producing a refractory material,



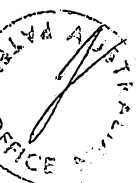
It is therefore an object of the present invention to provide a process for producing a refractory material and the refractory material produced thereby utilizing red muds to form high temperature and cryolite resistant refractories suitable for use as linings in aluminum production cells. The invention also has as one of its objectives the use of a refractory material lining, utilizing red muds as aforesaid in an aluminum electrolysis cell and a cell utilizing such a refractory material lining.

Accordingly the present invention provides a process for producing a refractory material which is resistant to corrosion by alkaline materials and fluorides at high temperature, which process comprises: calcining red mud containing Bayer sodalite at a temperature in the range of about 900 to 1400°C for a time sufficient to remove combined water and to produce nepheline from said Bayer sodalite in said red mud; grinding the product following calcination to the -4 Tyler mesh range; mixing the ground product with a binder, other than a clay, suitable for producing stable cryolite-resistant mineral phases in said refractory material, said binder being selected from the group consisting of silica-containing particulate materials or precursors thereof, alumina-containing particulate materials or precursors thereof, and mixtures thereof, in an amount sufficient to bind the ground product upon firing, and sufficient water to produce a formable mixture, wherein the amount of ground product and binder is such that the ratio of red mud to other ingredients is sufficient to provide a fired refractory material product which comprises at least 90% by weight of red mud, and wherein the alumina content of the ground product and binder is increased by addition, if necessary, so that it amounts to at least 10% more than that which becomes combined in nepheline formed in the refractory material; forming the mixture into a shaped product; and firing the shaped product at a temperature in the range of about 900 to 1400°C to produce said refractory material.



The present invention in a further aspect provides an aluminum eletrolysis cell comprising a container having a refractory lining holding cell contents which include a molten sodium compound, said lining comprising a refractory material which is resistant to corrosion by alkaline materials and fluorides at high temperature produced by: calcining red mud containing Bayer sodalite at a temperature in the range of about 900 to 1400°C for a time sufficient to remove combined water and to produce nepheline from said Bayer sodalite in said red mud; grinding the product following calcination to the -4 Tyler mesh range; mixing the ground product with a binder, other than a clay, suitable for producing stable cryolite-resistant mineral phases in said refractory material, said binder being selected from the group consisting of silica-containing particulate materials or precursors thereof, alumina-containing particulate materials or precursors thereof, and mixtures thereof, in an amount sufficient to bind the ground product upon firing, and sufficient water to produce a formable mixture; forming the mixture into a shaped product; and firing the shaped product at a temperature in the range of about 900 to 1400°C to produce said refractory material.

In a still further aspect, the present invention encompasses the use of a refractory material for lining an aluminum production cell, wherein said refractory material is a product produced by calcining red mud containing Bayer sodalite at a temperature in the range of about 900 to 1400°C for a time sufficient to remove combined water and to produce nepheline from said Bayer sodalite in said red mud; grinding the product following calcination to the -4 Tyler mesh range; mixing the ground product with a binder, other than a clay, suitable for producing stable cryolite-resistant mineral phases in said refractory material, said binder being selected from the group



- 1d -

consisting of silica-containing particulate materials or
precursors thereof, alumina-containing particulate
materials or precursors thereof, and mixtures thereof, in an
amount sufficient to bind the ground product upon firing,
and sufficient water to produce a formable mixture; forming
the mixture into a shaped product; and firing the shaped
product at a temperature in the range of about 900 to 1400°C
to produce said refractory material.

The binder would be a silica - and/or alumina

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5 ~~which comprises: calcining red mud; grinding the product~~
following calcination to the -4 Tyler mesh range; mixing
the ground product with a binder and sufficient water to
produce a formable mixture; forming the mixture into a
desired shape; and firing the shaped product to produce
said refractory material.

The invention also relates to the refractory materials
produced by the process and to the formable mixtures
~~produced as intermediate products.~~

10 ~~The binder is normally a silica and/or alumina-~~
containing particulate material that is capable of produc-
ing a formable mixture of satisfactory rheology and good
binding properties when mixed with the calcined red mud
particles and water. Moreover, the binder should also be
such that suitable stable cryolite-resistant mineral phases
are produced in the final fired product. Desirably, the
binder is somewhat acidic because this advantageously
reduces the basicity of the calcined red mud and improves
the bonding properties of the mixture upon firing. If
20 necessary, an acid or a base may be added to adjust the
pH to the desired level.

Suitable binders include colloidal silica, colloidal
alumina, sodium silicate and sodium aluminate. These
materials are all readily commercially available and any
commercial product may be employed. In the case of
colloidal silica, the product produced from fume silica is
preferred and SKW produces a suitable form of fume silica
for this purpose. Colloidal alumina in the form of a
liquid suspension (20 wt % alumina in about 80 wt % water)
30 can be obtained from Nyacol of Valley Forge, PA under the
trade mark NYACOL Al/20. Colloidal alumina in the form
of dry powder can be obtained from Vesta Chemical Co. of
Ponca City, OK under the trade mark CATAPAL. Sodium
silicate of various $\text{Na}_2\text{O}/\text{SiO}_2$ ratios can be obtained
35 from numerous suppliers, as can sodium aluminate.



The refractory products produced by at least the preferred forms of the inventive process are resistant at high temperatures to corrosion by alkaline materials and fluorides in oxidizing or reducing conditions. Indeed, as will be explained more fully later, certain forms of the products densify when exposed to such corrosive compounds (mainly sodium compounds) instead of being deteriorated. After such densification, the products are particularly resistant to dissolution by cryolite, mainly because of their low porosities.

Although the composition of red mud varies somewhat depending upon the source of bauxite and the processing conditions, a wide range of Bayer red muds can be used in the present invention. As will be explained more fully later, some of the red muds may benefit from the addition of compounds (e.g. alumina) so that nepheline (NaAlSiO_4) will be the main silicate phase produced on firing.

The analyses (on a dry weight basis) of some typical Bayer red muds are given in Table 1 below:

TABLE 1

COMPONENT	Red Mud from mixed BOKE and TROMBETAS bauxite % by wt	Red Mud from JAMAICAN bauxite % by wt	Red Mud from BOKE bauxite % by wt
Al_2O_3	20	12	20
Fe_2O_3	33	48	24
TiO_2	6	7	18
SiO_2	17	5	7
Na_2O	9	3	4
CaO	5	6	6
Loss on ignition at 1000°C	9	8	10
Other	1	11	11

Before use in the process described above, some pre-treatment of the red mud may be desirable, although the need for such a pre-treatment and the type of pre-treatment to be carried out depends on the red mud composition, the type of binder used and the product properties to be achieved.

Red mud normally contains sand (mainly silica) and soluble materials (e.g. NaOH , Na_2CO_3 and Na_2SO_4) which contribute to the material basicity, and pre-treatment may be required to vary the contents of these materials. For example, for red muds having an Al_2O_3 to SiO_2 ratio lower than about 1-1.5:1 (on a weight basis), it may be necessary to remove at least some of the sand (e.g. by filtering the red mud) to avoid the generation of free silica during the firing step and hence to provide good resistance to cryolite. It may also be necessary to wash the red mud in order to remove some of the soluble basic materials, for the following reasons.

The quantity of soluble materials in red mud contributing to material basicity is referred to as the "TTS" (total titrable soda) content. Typically, the TTS content of red muds is up to 10 % by wt (on a dry basis). When employing red muds of low TTS content (e.g. below 1.5 % by wt), and using binders such as colloidal silica (fume silica) or colloidal alumina, washing of the red mud may be required in order to reduce the basicity of the mixture sufficiently to permit the gelling of the binder necessary for the formation of a shapable intermediate product prior to firing. On the other hand, when employing red muds of high TTS content (e.g. 1.5 to 10% by wt), no washing may be required because the calcined red mud may then contain sufficient reactive Na_2O to produce from binders such as colloidal silica or colloidal alumina cementing compounds such as sodium silicate or sodium aluminate, respectively.

After the pre-treatment steps of sand removal and washing, if required, the main process steps are carried out.

5 The steps of calcining and grinding the red mud result in the formation, after the firing step, of refractory products which can resist harsh environments, such as those encountered in aluminum production cells, and which are resistant to cracking. The grinding step has the effect of providing fired products of desirable specific surface areas and densities. The calcination step has the effect of pre-shrinking the red mud so that, during the firing step, shrinkage is generally less than 1% by volume and cracking is reduced. The calcination step also has the effect of removing the combined water and of modifying the sodium salts included in the Bayer sodalite (which is 15 a main constituent of red muds and is a compound consisting mainly of Al_2O_3 , SiO_2 and Na_2O , but sometimes also containing Na_2CO_3 and Na_2SO_4). After calcination, the red mud particles include nepheline (NaAlSiO_4) which is the main silicate phase so produced. Based on the ternary Na_2O - Al_2O_3 - SiO_2 phase diagram, reaction products of nepheline and Na_2O (the major source of corrosion of the potlining in aluminum production cells) lead to the formation of eutectic compounds having melting points higher than 915°C. 25 Moreover, it has been found that by starting with a red mud of a sufficiently high alumina content (i.e. one containing at least about 10% more than the quantity of alumina which becomes combined in the nepheline in the calcined product), or by supplementing the alumina content of low-alumina red mud to form a starting material of similar high alumina content, it can be ensured that nepheline will be formed predominantly as the silicate phase and that the reaction products will then remain in the solid state until temperatures reach at least 955°C. The added alumina, 35 when employed, is preferably in the form of particles of -65 Tyler mesh and can be added to the red mud either before or after the calcination step. In the

latter case, the alumina becomes incorporated into the nepheline during the final firing step.

5 The calcination is generally carried out in air at a temperature and for a time suitable to bring about the changes indicated above. Preferably, the calcination is carried out at a temperature in the range of about 900-1400°C and more preferably 1,000 to 1,200°C, for a time of about 5 to 10 hours. Following calcination, the red mud is cooled and then ground to the -4 Tyler mesh range. The particular granulometry within this range can be selected (e.g. by screening) to produce a product after firing of the density and specific surface area desired for the purposes which will be apparent later.

10 Following grinding, the particulate product is mixed with the binder, and preferably sufficient water, to produce a formable mixture.

15 The binder can be added to the calcined red mud as a dry powder followed by water addition, or the binder may be premixed with water and then mixed with the red mud particles. In the latter case, further water addition may or may not be necessary in order to give a product of the desired formability.

20 The amount of binder employed usually falls within the range of 2 to 8% solids by weight based on the dry weight of the calcined product. The amount of binder employed controls the mechanical properties of the final product (see Example 5 below). The amount of water employed depends upon the forming process to be employed and should be just enough to give the mixture the proper consistency
25 30 required for the forming process.

35 In addition to the binder, other additives may be mixed with the calcined red mud. As noted above, it may be desirable to add alumina to increase the overall alumina content of the product to at least about 10% more than that which becomes combined in the nepheline in the fired product. This may be achieved simply by using colloidal alumina as a binder, but further alumina may be added

(not necessarily in colloidal form but generally of -65 Tyler mesh size) if desired. Other additives may be used to improve sintering on firing or resistance to chemicals. Examples of such other additives are sodium oxide, aluminum fluoride, sodium fluoride, sodium carbonate and sodium sulfate. Sodium carbonate and sodium sulfate can improve sintering during firing and also act as a source of Na_2O which may be required for reasons explained later.

It is most desirable that the resulting mixture should contain at least (and preferably more than) 90% by weight of red mud. That is, the amount of binder and additives (excluding water) mixed with the red mud should preferably total no more than 10% by weight of the mixture (on a solids basis) prepared for firing.

The resulting mixture can be formed prior to firing into any desired shape (e.g. tiles, bricks or slabs) by well-known means such as pressing, casting (with or without vibrating), extrusion or injection moulding. Following shaping in this way, the product is preferably cured at room temperature for up to about 24 hours, dried e.g. by heating to 110-120°C for about 24 to 48 hours and is finally fired at 900-1400°C, and preferably at 1000°C - 1200°C, for about 5 to 10 hours.

As an alternative to the formation of fired refractory products of predetermined shapes, the mixtures of ground calcined red mud and binder may be produced and sold as monolithics, which include mortars and castables. The purchaser may then use the monolithics by ramming or tamping them into place, or by casting them into desired shapes, followed by curing, drying and firing the mixture in the manner indicated above. The mixtures sold for this purpose need not contain water since the purchaser can add water immediately prior to their use.

The fired products produced by the invention can be used for a variety of purposes requiring high temperature resistant materials, but are particularly suited for use in the linings of aluminum production cells because of

their high resistance to the extremely corrosive cryolitic species present in such cells.

Improved insulating properties can be imparted to the fired products of the invention by including heat-consumable particles, e.g. polystyrene spheres, etc., into the mixtures of calcined red mud particles and binder. During the firing step, the particles are consumed, leaving a foam-like insulating, light-weight refractory structure. For example, the thermal conductivity of the product may be reduced to around 0.15 w/m°C by adding less than 5% by weight of polystyrene spheres to the starting raw materials.

It has unexpectedly been found that a particular group of the fired products of the invention exhibit "self-densification" (i.e. a substantial reduction of porosity) when exposed to solid cryolite, cryolite-NaF mixtures or other source of sodium such as NaCl at a temperature of around 850°C or above, e.g. when used in an aluminum production cell. The particular group of the fired products includes all those having the following ratio between 0.05 and 1, exclusively (i.e. those products for which $0.05 < R < 1$):

$$R = \frac{\text{Na}_2\text{O}}{\text{SiO}_2} \cdot S$$

wherein: Na_2O = the molar fraction of Na_2O in the product originating from the decomposition of the soluble salts in the red mud during calcination (which is approximately 0.8 TTS wt % of the calcined red mud fraction in the product) and from the binder (e.g. if sodium silicate is used) and/or from additives such as Na_2CO_3 and Na_2SO_4 .

SiO_2 = the molar fraction of SiO_2 in the product originating from the binder when a siliceous binder is used (e.g. colloidal silica, fume silica or sodium silicate);

S = the ratio of specific surface area (SSA) of the calcined red mud particles to the maximum SSA value which is obtained from the -65 mesh material (the finer material in the product), i.e. $S=1$ if 100% of -65 mesh particles are used.

In contrast, products of the invention having an R ratio equal to 0.05 or less or 1 or more do not self-densify at any temperature.

Those products for which $0.05 < R < 1$ can achieve porosities of 10% or less upon exposure to solid cyrolite at temperatures around 850°C or higher. For given values of Na_2O and SiO_2 , the ratio R can be adjusted as required by controlling the specific surface area (SSA) of the calcined red mud particles. The maximum SSA is achieved by using only -65 Tyler mesh calcined red mud particles. Lower SSA are achieved from a granulometric distribution of calcined red mud including coarser particles (e.g. a mixture of the following fractions : -4 + 10, -10 + 28, -28 + 65 and -65 Tyler mesh). Alternatively, the R ratio can be adjusted by varying the amount of binder (SiO_2) and/or by adding Na_2O -rich additives (e.g. Na_2CO_3 , Na_2SO_4 etc) to the red mud before or after calcination.

If it is desired to make $R \leq 0.05$, this can normally be done by:

- (a) washing the mud
- (b) using coarse red mud particles
- (c) using higher silica binder contents.

If it is desired to make $R \geq 1$, this can normally be done by:

- (a) using unwashed high TTS content red muds or by using low TTS content red muds plus additives such as Na_2CO_3 and Na_2SO_4
- (b) using only -65 Tyler mesh particles ($S=1$)
- 5 (c) using lower silica binder contents.

It will be noted that the above definition of the R ratio is for those cases in which a siliceous binder is used. When colloidal alumina is used as the binder, it is believed that self-densifying products can also be formed but the values of the corresponding R ratio and the
10 temperature at which self densification takes place may be different.

Self-densification appears to result from a filling of the pores of the product by sodium components. These
15 sodium components then appear to become linked to the nepheline (NaAlSiO_4) matrix of the product and thus increase the density of the product without causing any shrinkage. The self-densification effect reduces the porosity of the product, which is particularly advantageous when the refractory product is used in aluminum production
20 cells because attack by the cell contents is thereby substantially reduced.

The products of the invention can be used to line the entire cell (or "pot") of aluminum production cells,
25 including the protective barrier, the intermediate and the insulating layers. The protective barrier may utilize the products for which $0.05 < R < 1$ which will self-densify upon sodium absorption (mainly NaF) from the cryolitic bath. If desired, those products could be densified prior to installation by pre-exposing them to solid cryolite (or
30 other source of sodium) at more than about 850°C . The intermediate and insulating layers may involve the products for which $R \leq 0.05$ or $R \geq 1$. Those products cannot densify upon sodium component absorption, at any temperature, and
35 could give a thermal conductivity of both layers of around 0.35 to $0.55 \text{ w/m}^\circ\text{C}$ (about 3 times less than the densified products). However, even the insulating layer may comprise

the products for which $0.05 < R < 1$ if they are not exposed to temperatures above about 850°C . In such cases, densification will not proceed in that layer and thermal conductivity of the products will still fall in the above range.

5 If required, the insulating layer can involve the lightweight modified products, for even better insulation.

The following Examples illustrate the invention in further detail, but should not be regarded as limiting the scope of the invention in any way.

10 Example 1

The following procedure was carried out to demonstrate the self-densification property of products made from red mud of low TTS content.

Samples were prepared by removing sand from red mud, washing the mud to reduce the TTS content to 0.5 wt % (on a dry basis) filtering it, calcining it at 1000°C for five hours (which gave the chemical and mineralogical composition shown in Table 2 below), grinding it to specific particle sizes and then mixing it with 4% by weight of fume silica (-65 Tyler mesh) and water to form a mixture containing about 34% by weight of water. The mixture was shaped by pressing at 4000 psi small cylindrical pieces having a diameter of about 3.84 cm and a height of about 2.5 cm, dried and then fired at 1000°C for five hours.

25 The samples were exposed to 60:40% by weight cryolite- NaF mixture for five hours at temperatures from 850°C to 880°C (the mixture being in the solid state at these temperatures).

TABLE 2

Chemical and mineralogical compositions of
the calcined red mud used, after sand removal,
washing and filtering

	COMPOSITION (in wt)
<u>Chemical Constituents</u>	
Fe ₂ O ₃	30%
Al ₂ O ₃	22%
SiO ₂	19%
TiO ₂	7%
Na ₂ O	10%
CaO	1%
Others	11%
<u>Mineralogy</u>	
Hematite (Fe ₂ O ₃)	Major*
Nepheline (NaAlSiO ₄)	Mean*
Pseudo Brookite (Fe ₂ TiO ₃)	Mean*
Others	Trace*

* With respect to the relative peak intensities recorded
on the spectrum from XRD analysis.

The results are summarized in Table 3 below.

TABLE 3

Degree of Densification of products made from red mud of low TTS content in Solid 60:40 Wt % Cryolite-NaF Mixture, at Various Temperatures, with respect to their "R" ratio value.

Granulometric Distribution	Wt. % of particles of indicated sizes	
	R = 0.10*	R = 0.03*
-10 + 28 mesh	0	40
-28 + 65 mesh	0	27
-65 mesh	100	33
S**	1.0	0.33
Treatment Temperatures	% Loss in Porosity	
850°C	2	2
860°C	2	0
870°C	40	10
880°C	75	5

$$* R = \frac{Na_2O \cdot S}{SiO_2} \approx \frac{(0.8 \text{ TTS}) S}{SiO_2}$$

** Based on calculation.

The samples having the higher R ratio value ($R = 0.1$, which is in the range of $0.05 < R < 1$), i.e. those produced from the finer particles, exhibited densification by sodium absorption at temperatures above 860°C . At 880°C , a 75% reduction in porosity took place in one sample. This resulted in a final porosity of less than 10%. This is lower than the porosity of most commercial refractories which is normally at least 15% and more generally between 20 and 25%.

Samples having the R ratio value near 0 ($R=0.03$), i.e. those produced from coarser red mud particles, did not exhibit significant densification at any temperatures.

Example 2

The following procedure was carried out to demonstrate the self-densification property of products made from red mud of high TTS content.

Samples were prepared by removing sand from red mud but without washing it to keep its original TTS content after the Bayer circuit (varying between 2.5 and 2.9 wt % (on a dry basis)). Then the mud was filtered, calcined at 1000 to 1100°C for 5 to around 10 hours, ground to obtain specific particles sizes and finally mixed with 2 to 6 wt % fume silica (~ 65 Tyler mesh) and enough water (between 20 to 30 wt % of the dry mixture) to be shaped by vibration casting into molds. The samples were exposed to the same cryolithic mixture than in Example 1, at 880°C for 24 hours.

The results are summarized in Table 4. Self-densification took place for each sample, their "R" ratios being within the range $0.05 < R < 1$.

TABLE 4

Degree of Densification of products made from red mud of high "TTS" content, in solid 60:40 wt % cryolite - NaF mixture, at various temperatures, with respect to their "R" ratio value in the range $0.05 < R < 1$.

PRODUCT COMPOSITION	1	2	3	4	5
-4 +10 mesh	22%	0%	37%	37%	0%
-10 +28 mesh	34%	4%	26%	26%	0%
-28 +65 mesh	14%	27%	9%	9%	0%
-65 mesh	30%	69%	27%	27%	100%
Silica fumes	4%	6%	4%	2%	4%
TTS	2.9%	2.7%	2.5%	2.5%	2.5%
S*	0.18	0.70	0.14	0.14	1.0
R**	0.10	0.25	0.07	0.14	0.5
Lost in porosity @densification	33%	19%	34%	23%	45%

* Based on calculations

$$** R = \frac{Na_2O}{SiO_2} \cdot S \approx \frac{(0.8 \text{ TTS}) S}{SiO_2}$$

Example 3

The same sample submitted to the test described in Example 1, showing the highest densification (e.g. a reduction of 75% of the initial porosity after 5 hours at 1000°C) was then contacted with liquid cryolite and exhibited very good stability. Indeed, the corrosion was much less than for a medium duty firebrick subjected to the same conditions, and no eutectic liquids as reaction products were observed.

Example 4

Samples made by the same procedure as in Example 1, but shaped by vibration casting in 22.86 x 11.43 x 6.35 cm standard molds, were exposed to liquid aluminum for 5 hours at 900°C. Compared to a medium duty firebrick tested in the same conditions, the stability of the product was better.

Also, similar samples were tested in Al-5 wt % Mg for 96 hours and compared to 18 aluminosilicate castables ranging from 38.61 to 82.50 wt % in alumina content. Based on the extent of wettability, penetration and chemical reactions by the alloy, the resistance to corrosion of the samples were classified from 1 to 6 (i.e. good resistance to no resistance, respectively). Only 26% of the overall samples tested were classified no. 1, including the red mud product.

Example 5

The following procedure was carried out to demonstrate the effect of binder content on the physical properties of the red mud products.

Samples were prepared according to Example 2 and tested for their bulk density, apparent porosity, cold crushing strength and room temperature thermal conductivity. The results are summarized in Table 5.

Upon increasing the amount of fume silica from 2 to 8 wt %, the product cold crushing strength and thermal conductivity increased from 6.7 to 26.1 MPa and from 0.46 to 0.63 W/mk, respectively.

TABLE 5

Effect of fume silica binder content on the physical properties of the red mud products

<u>Products Composition, wt %</u>				
Red mud	98	96	94	92
Fume silica	2	4	6	8
<u>Physical Properties</u>				
Bulk density, g/cm ³	1.62	1.63	1.69	1.74
Porosity, %	45	40	38	37
Cold crushing strength, MPa	6.7	14.8	21.0	26.1
Room temperature thermal conductivity, W/mk	0.46	0.50	0.55	0.63

Example 6

During the dry mixing step of samples made by the same procedure as in Example 2, using 4 wt % fume silica, 1 wt % polystyrene spheres of less than 2 mm in diameter were added. The results of thermal conductivity tests showed a reduction of around 35 % compared to products free of that additive.

Example 7

The following gives some examples of red mud from Brazilian, Japanese and Australian plants (see Table 6) that may not need sand removal nor alumina addition to convert them into refractory products which can meet the chemical requirements for use in potlining of alumina reduction cells at temperatures up to 955°C.

Each of the red mud composition given in Table 6 already contains at least 10% more than the amount of alumina required to generate Nepheline (NaAl SiO_4) on firing as the main silicate phase (no free silica).

TABLE 6

Component	Red mud from one Brazilian Plant, % by wt	Red mud from one Japanese Plant, % by wt	Red mud from one Australian Plant, % by wt
Al ₂ O ₃	17	21	23
Fe ₂ O ₃	50	35	35
TiO ₂	6	2	8
SiO ₂	10	15	16
Na ₂ O	4	9	9
CaO	3	0.5	2
Loss on ignition at 1000°C	8	15	7
Other	2	2.5	0

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A process for producing a refractory material which is resistant to corrosion by alkaline materials and fluorides at high temperature, which process comprises: calcining red mud containing Bayer sodalite at a temperature in the range of about 900 to 1400°C for a time sufficient to remove combined water and to produce nepheline from said Bayer sodalite in said red mud; grinding the product following calcination to the -4 Tyler mesh range; mixing the ground product with a binder, other than a clay, suitable for producing stable cryolite-resistant mineral phases in said refractory material, said binder being selected from the group consisting of silica-containing particulate materials or precursors thereof, alumina-containing particulate materials or precursors thereof, and mixtures thereof, in an amount sufficient to bind the ground product upon firing, and sufficient water to produce a formable mixture, wherein the amount of ground product and binder is such that the ratio of red mud to other ingredients is sufficient to provide a fired refractory material product which comprises at least 90% by weight of red mud, and wherein the alumina content of the ground product and binder is increased by addition, if necessary, so that it amounts to at least 10% more than that which becomes combined in nepheline formed in the refractory material; forming the mixture into a shaped product; and firing the shaped product at a temperature in the range of about 900 to 1400°C to produce said refractory material.



2. A process according to claim 1 wherein the calcination is carried out at a temperature in the range of 1000-1200°C for a period of about 5-10 hours.

3. A process according to claim 1 wherein the firing of the shaped product is carried out at a temperature in the range of 1000-1200°C for a period of about 5-10 hours.

4. A process according to claim 1, claim 2 or claim 3 wherein the binder is selected from the group consisting of colloidal silica, colloidal alumina, sodium silicate and sodium aluminate.

5. A process according to claim 1 wherein said binder is a siliceous material and said mixture prior to firing has a value of R in the range of $0.05 < R < 1$, wherein $R = \frac{Na_2O \cdot S}{SiO_2}$

and wherein: Na_2O = the molar fraction of Na_2O in the product originating from the decomposition of soluble salts in the red mud during calcination and from the binder and/or and from additives;

SiO_2 = the molar fraction of SiO_2 in the product originating from the binder;

S = the ratio of specific surface area (SSA) of the calcined red mud particles to the maximum SSA value which is obtained from -65 Tyler mesh calcined red mud material.



6. A process according to claim 5 which further comprises contacting the fired shaped product with a solid sodium compound at a temperature of about 850°C or higher.

7. A process according to claim 6 wherein the sodium compound comprises cryolite.

8. A process according to claim 6 wherein the sodium compound comprises a mixture of cryolite and NaF.

9. A process according to claim 1, claim 2 or claim 3, wherein the calcined red mud, following grinding, contains particles in each of the following size ranges: -4 +10 Tyler mesh, -10 +28 Tyler mesh, -28 +65 Tyler mesh and -65 Tyler mesh, said particles forming up to 37%, up to 34%, up to 27% and at least 27% by weight, respectfully, of the calcined red mud.

10. A process according to claim 1, claims 2 or claim 3 wherein the amount of said binder mixed with said ground product is in the range of 2 to 8% by weight solids based on the dry weight of the calcined red mud.

11. A process according to claim 1, claim 2 or claim 3 wherein said ground product is additionally mixed with an additive selected from the group consisting of alumina, sodium oxide, aluminum fluoride, sodium fluoride, sodium carbonate and sodium sulfate.

12. A process according to claim 1, claim 2 or claim 3 wherein said mixture, after being formed into a desired shape, is first cured by being allowed to stand at room temperature for several hours and is then dried by being heated at about 110-120°C for several hours, before being subjected to said firing step.



13. A process according to claim 1, claim 2 or claim 3 wherein the particles of heat-gasifiable material are mixed with said ground product, binder and water prior to forming said mixture into said desired shape, the amount of heat-gasifiable material being sufficient to increase the heat insulation of the refractory material produced by firing said mixture compared to mixtures containing no such heat-consumable material.

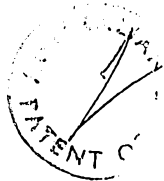
14. A process according to claim 1, claim 2 or claim 3 wherein the free silica content of the red mud is minimized by sand removal prior to said calcination step.

15. A process according to claim 1, claim 2 or claim 3 wherein soluble basic compounds are at least partially removed from the red mud by washing prior to said calcination step.

16. A refractory material which is resistant to corrosion by alkaline materials and fluorides at high temperature, prepared by a process according to any preceding claim.

17. A refractory material of low porosity which is resistant to corrosion by alkaline materials at high temperature, prepared by a process according to claim 6, claim 7 or claim 8.

18. An aluminum electrolysis cell comprising a container having a refractory lining holding cell contents which include a molten sodium compound, said lining comprising a refractory material which is resistant to corrosion by alkaline materials and fluorides at high



temperature produced by: calcining red mud containing Bayer sodalite at a temperature in the range of about 900 to 1400°C for a time sufficient to remove combined water and to produce nepheline from said Bayer sodalite in said red mud; grinding the product following calcination to the -4 Tyler mesh range; mixing the ground product with a binder, other than a clay, suitable for producing stable cryolite-resistant mineral phases in said refractory material, said binder being selected from the group consisting of silica-containing particulate materials or precursors thereof, alumina-containing particulate materials or precursors thereof, and mixtures thereof, in an amount sufficient to bind the ground product upon firing, and sufficient water to produce a formable mixture; forming the mixture into a shaped product; and firing the shaped product at a temperature in the range of about 900 to 1400°C to produce said refractory material.

19. A cell according to claim 18 wherein the ratio of red mud to other ingredients in said lining is at least 90% by weight.

20. A cell according to claim 18 wherein the alumina content of the lining is at least 10% more than that combined in nepheline present in said refractory material.

21. A cell according to claim 18 wherein said binder is a silica-containing material or precursor thereof and said mixture prior to firing has a value of R in the range of $0.05 < R < 1$, wherein $R = \frac{\text{Na}_2\text{O} \cdot \text{S}}{\text{SiO}_2}$

and wherein: Na_2O = the molar fraction of Na_2O in the product originating from the decomposition of soluble salts in the



red mud during calcination and from the binder and from any additives added to said ground product.

SiO_2 = the molar fraction of SiO_2 in the product originating from the binder;
S = the ratio of specific surface area (SSA) of the calcined red mud particles to the maximum SSA value which is obtained from -65 Tyler mesh material.

22. The use of a refractory material for lining an aluminum production cell, wherein said refractory material is a product produced by calcining red mud containing Bayer sodalite at a temperature in the range of about 900 to 1400°C for a time sufficient to remove combined water and to produce nepheline from said Bayer sodalite in said red mud; grinding the product following calcination to the -4 Tyler mesh range; mixing the ground product with a binder, other than a clay, suitable for producing stable cryolite-resistant mineral phases in said refractory material, said binder being selected from the group consisting of silica-containing particulate materials or precursors thereof, alumina-containing particulate materials or precursors thereof, and mixtures thereof, in an amount sufficient to bind the ground product upon firing, and sufficient water to produce a formable mixture; forming the mixture into a shaped product; and firing the shaped product at a temperature in the range of about 900 to 1400°C to produce said refractory material.

23. The use of a refractory material according to claim 22 wherein the ratio of red mud to other ingredients in the material is at least 90% by weight.



24. The use of a refractory material according to claim 22 or claim 23 wherein the alumina content of the material is at least 10% more than that combined in nepheline present in the refractory material.

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