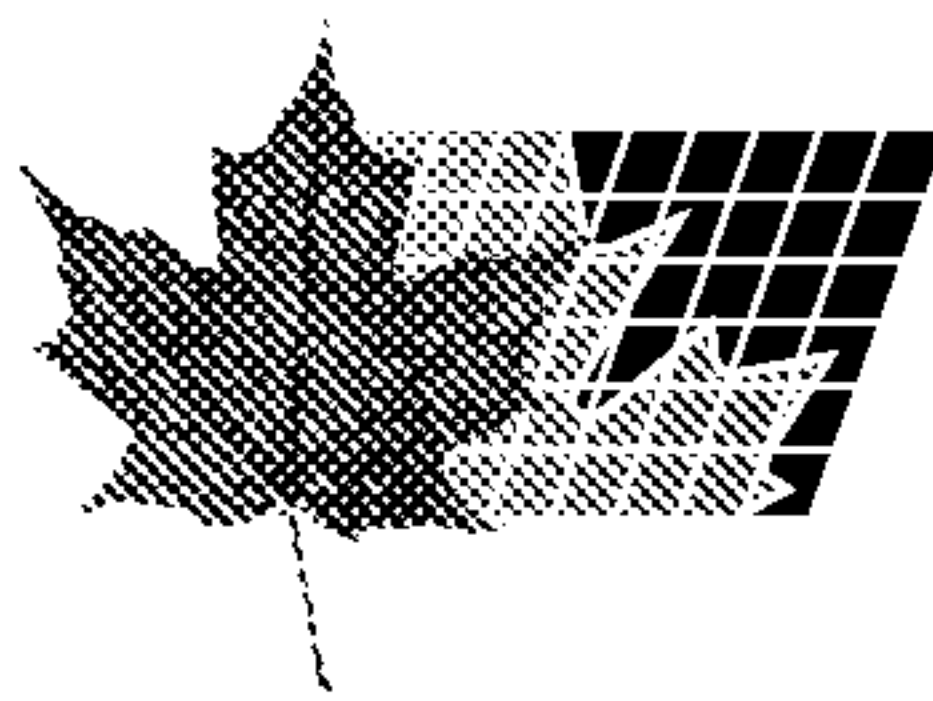




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(54) **PROCEDE DE PRODUCTION DE FIBRES VITREUSES**

(54) **PROCESSES FOR THE PRODUCTION OF MAN-MADE
VITREOUS FIBRES**

(57) La présente invention concerne des fibres vitreuses contenant au moins 14% d'aluminium. Le procédé consiste à prendre une charge de matière minérale brute contenant des scories de ferrochrome, et à la mettre dans un four. Les scories représentent de préférence 5% de la masse de la matière minérale brute. Le procédé consiste ensuite à faire fondre la charge dans le four pour obtenir un bain de fusion, puis à fibériser le bain de façon à former les fibres.

(57) Man-made vitreous fibres having a content of aluminium of at least 14 % are produced by providing a charge of raw mineral material which contains ferro-chromium slag, preferably at least 5 % by weight ferro-chromium slag, in a furnace, melting the charge in the furnace to form a melt and fiberising the melt to form fibres.

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(54) Title: PROCESSES FOR THE PRODUCTION OF MAN-MADE VITREOUS FIBRES (57) Abstract Man-made vitreous fibres having a content of aluminium of at least 14 % are produced by providing a charge of raw mineral material which contains ferro-chromium slag, preferably at least 5 % by weight ferro-chromium slag, in a furnace, melting the charge in the furnace to form a melt and fiberising the melt to form fibres.		

**Processes for the Production of
Man-Made Vitreous Fibres**

This invention relates to the production of man-made vitreous fibres (MMVF) having high content of alumina.

5 MMVF may be made by forming a mineral melt by melting a mineral charge in a furnace and fiberising the melt, usually by a centrifugal fiberising process.

There is a particular interest in the manufacture of MMVF insulation containing more than 14%, and often 18 to
10 30%, alumina, for instance as described in W096/14274 and W096/14454.

In many of the furnaces which are used, there is a large pool of melt and the mineral charge is melted into this pool. Examples are tank and electric furnaces. Melting
15 of material is conducted into a large volume of previously melted material and the residence time of charge material in the melt pool tends to be relatively long, typically several hours.

However, there is another type of furnace which is
20 used for forming the melt for MMVF production, especially for fibres of the types that are referred to as rock (including stone or slag) fibres. This is a shaft furnace in which the furnace contains a self-supporting column of solid coarse mineral material and combustion gases permeate
25 through this column so as to heat it and cause melting. The melt drains to the bottom of the column, where a pool of melt is usually formed. The melt is removed from the base of the furnace. In this case the pool of melt is relatively small and the residence time of material in that pool is
30 relatively short, typically minutes.

Certain materials have been suggested as suitable for provision of the above-discussed high alumina fibres. These include minerals which have high aluminium content such as bauxite. However, bauxite and other high aluminium
35 materials, particularly those having high content of alumina Al_2O_3 , have high melting point and tend to melt only slowly into the pool of melt. Bauxite in particular tends

to dissolve into the melt rather than melt completely. It may dissolve or melt incompletely and leave a residue at the base of the furnace, which must be removed from time to time. Thus to improve the melting fuel, usually solid fossil fuel, is generally included with the charge to provide energy for the melting process. Greater amounts of fuel lead to greater costs.

Thus the invention is concerned with the problem of providing a process for the production of high aluminium content fibres which alleviates melting problems in an economic manner. These problems are particularly noticeable in shaft furnaces but it would be desirable to improve melting in all types of furnace.

According to the invention we provide a process of producing man-made vitreous fibres (MMVF) having a content of at least 14% aluminium, measured as wt.% Al_2O_3 , by providing a charge of raw mineral material in a furnace, melting the charge in the furnace to form a melt and fiberising the melt to form fibres, characterised in that the charge comprises ferro-chromium slag.

We find that the inclusion of this one particular type of starting material, out of the entire range of waste and virgin materials which exist, and in contrast to many of the materials known for the production of high aluminium MMVF, such as bauxite, allows the provision of a high level of aluminium but alleviates melting problems. It is believed that this is related to the fact that aluminium in the form of, say, bauxite is very difficult to melt and requires major energy input, whereas ferro-chromium slag materials are produced by a process which results in the aluminium being present in a form which requires less energy input for melting. Additionally, the resultant content of chromium in the fibres can even have beneficial effects.

The invention is further beneficial in that it alleviates the melting problem by using a source of

aluminium which is economical, conveniently available and for which previously there were no or very limited uses.

Ferro-chromium slag is obtained from the metallurgical industry, in particular the ferro-alloy industry. It is produced as a by-product from the formation of ferro-chromium alloy. Suitable materials have content of aluminium from 15 to 40%, preferably 20 to 35%, more preferably at least 22% and in particular 24 to 32%. They have content of iron from 1 to 10%, preferably 2 to 7%. Content of chromium is preferably from 4 to 15%, more preferably 5 to 13%. All proportions are measured by weight based on the oxide.

The fibres produced according to the invention have high content of aluminium, namely at least 14% measured as Al_2O_3 based on weight of oxides. Suitable high aluminium, biologically soluble, fibres which can advantageously be made in the present invention are described in WO96/14454 and WO96/14274. Others are described in WO97/29057, DE-U-2,970,027 and WO97/30002. Reference should be made to each of these. In general the fibres and the melt from which they are formed have an analysis (measured as % by weight of oxides) within the various ranges defined by the following normal and preferred lower and upper limits:

SiO_2 at least 30, 32, 35 or 37; not more than 51, 48, 45 or 43

Al_2O_3 at least 14, 15, 16 or 18; not more than 35, 30, 26 or 23

CaO at least 2, 8 or 10; not more than 30, 25 or 20

MgO zero or at least 2 or 5; not more than 25, 20 or 15

FeO (including Fe_2O_3) zero or at least 2, 5; not more than 15, 12 or 10

$\text{FeO} + \text{MgO}$ at least 10, 12, 15; not more than 30, 25, 20

$\text{Na}_2\text{O} + \text{K}_2\text{O}$ zero or at least 1; not more than 19, 14, 10

$\text{CaO} + \text{Na}_2\text{O} + \text{K}_2\text{O}$ at least 10, 15; not more than 30, 25

TiO_2 zero or at least 1; not more than 6, 4, 2

$\text{TiO}_2 + \text{FeO}$ at least 4, 6; not more than 18, 12

B_2O_3 zero or at least 1; not more than 5, 3

P_2O_5 zero or at least 1; not more than 8, 5
Others zero or at least 1; not more than 8, 5

The fibres preferably have a sintering temperature above 800°C, preferably above 1000°C.

5 The melt preferably has a viscosity at fibre forming temperature of 5 to 100 poise, preferably 10 to 70 poise at 1400°C.

The fibres preferably have an adequate solubility in lung fluids as shown by in vivo tests or in vitro tests, typically conducted in physiological saline buffered to about pH 4.5. Suitable solubilities are described in WO96/14454. Usually the rate of dissolution is at least 10 or 20nm per day in that saline.

15 The preferred fibres which are made in the invention have an analysis which contains at least 15%, usually at least 17% and most usually at least 18% Al_2O_3 , e.g., up to 30, 35 or 40%.

Particularly preferred fibres produced according to the invention are biologically soluble fibres containing 30 to 51% SiO_2 , 18 to 30% Al_2O_3 , 2 to 30% CaO , 0 to 25% MgO , 0 to 15% FeO , 0 to 6% TiO_2 , 0 to 6% P_2O_5 , 0 to 5% B_2O_3 , 0 to 10% alkali metal oxide and 0 to 8% other elements. Particularly preferred fibres are those described in, for instance, WO96/14454 and WO96/14274. The fibres preferably have physiological solubility as described therein.

25 The use of ferro-chromium slag as a starting material tends to result in a measurable content of chromium in the final fibres. The amount of chromium is usually from 0 to 2%. Preferred amounts of chromium are from 0.6 to 1%. We find that the inclusion of chromium is not harmful to insulation or solubility and can in fact have positive advantages. For instance, it may give a fungicidal effect. This can be useful in any permanently installed material such as MMVF products. Thus the final fibres may have fungicidal properties.

35 Content of chromium and solubility can be assessed by measuring dissolution rate in the same way as described

above except in an aqueous medium which is aqueous oxalic acid at pH 2.5. Under such conditions the fibres produced in the invention preferably give a solution containing from 10 to 20 ppm chromium.

5 The fibres produced in the invention have high aluminium content. Preferably at least 15%, more preferably at least 20% and in some cases at least 25% (based on total aluminium content measured as above), of the aluminium content is provided by ferro-chromium slag.

10 The fibres may be made in standard manner, by forming a mineral melt by melting mineral solids which include the ferro-chromium slag material and then forming fibres from the melt, often by a centrifugal fibre formation process.

For instance the fibres may be formed by a spinning
15 cup process in which they are thrown outwardly through perforations in a spinning cup, or melt may be thrown off a rotating disc and fibre formation may be promoted by blasting jets of gas through the melt. Preferably fibre formation is conducted by pouring the melt onto the first
20 rotor in a cascade spinner. Preferably the melt is poured onto the first of a set of two, three or four rotors, each of which rotates about a substantially horizontal axis whereby melt on the first rotor is primarily thrown onto the second (lower) rotor although some may be thrown off
25 the first rotor as fibres, and melt on the second rotor is thrown off as fibres although some may be thrown towards the third (lower) rotor, and so forth.

The melt may be formed in any conventional manner, for instance using the furnaces discussed above having a large
30 pool of melt into which mineral charge is melted, such as tank and electric furnaces. However, the invention is particularly beneficial in furnaces in which the residence time of the raw materials in the melt is much shorter, such as shaft furnaces in which the furnace contains a column of
35 solid mineral material. The melt drains to the bottom of the column, usually into a pool of melt, and is removed

from the base of the furnace. Preferred shaft furnaces are cupola furnaces.

The ferro-chromium slag may be incorporated in the charge in any convenient form. It may be added as coarse lumps which are added directly to the furnace. It may be added, after conversion to a suitably small particle size, in the form of bonded briquettes which are then added to the furnace.

Generally at least 5%, preferably at least 10 or 15%, and in particular at least 20%, of the total charge is ferro-chromium slag. Normally the amount is not more than 50%, in particular not more than 30% (all percentages by weight based on the mineral charge which forms the melt). Briquettes, if they are used and contain ferro-chromium slag, preferably contain at least 5%, more preferably at least 10, 15 or 20%, ferro-chromium slag, but not usually more than 30 or 50%.

The remainder of the charge may be conventional, for instance virgin rock or recycled MMVF products. Waste material may also be used.

Wastes that can conveniently be incorporated as well as the ferro-chromium slag include other slags from the metallurgical industry, especially steelmaking slags such as converter slags, ladle slags or EAF slags, and other slags from the ferro-alloy industry such as ferro-manganese and ferro-silicon slags; slags and residues from the primary production of aluminium, such as spent aluminium pot lining or red mud; sewage sludge; bleaching clay; residues from the incineration of household and industrial wastes, especially slags or filter ashes from the incineration of municipal solid wastes; glass waste (or slags) from the vitrification of other waste products; glass cullets; waste products from the mining industry, especially minestone from the excavation of coal; residues from the incineration of fossil fuel, especially from the combustion of coal at power plants; spent abrasive sand; spent moulding sand from iron and steel casting; waste

sieving sand; and breakage waste from the ceramic and brick industry. Toxic virgin rock may also be used as waste. Other preferred wastes include slags and residues from the secondary production of aluminium. These are often generically described as "aluminium dross" or "aluminium oxide dross". Preferred wastes contain 0.5 to 10 wt.% metallic aluminium and 50 to 90 wt.% alumina. They are discussed, for use in briquettes, in our copending application number.... filed today, reference PRL04162WO.

10 In particular we prefer to use wastes from the aluminium casting process. This process provides a particular alumina-rich waste material described as "alu-dross". This tends to contain significant proportions of metallic aluminium and is thus treated in order to retrieve the

15 metallic aluminium. The alu-dross is generally crushed, milled and sieved. This produces some aluminium for re-sale and an aluminium-rich fraction which is sent to a furnace for re-use. As a by-product an alumina-rich powder is also produced. This is described herein as "crushed alu-dross".

20 The aluminium-rich fraction, optionally together with other aluminium-containing waste materials, is subjected to remelting in a furnace. This may be a rotating furnace or kiln. The aluminium waste may be subjected to plasma heating. A conventional furnace may also be used. Salt is

25 usually added to the furnace in order to reduce the surface tension of the aluminium and reduce oxidation. This process produces an aluminium fraction for re-sale, more alu-dross and a salt slag material. The salt slag can be subjected to a wet chemical process (involving water washing and high

30 temperature treatment) which produces a salt fraction, which is recycled to the furnace, and a further alumina-rich powder, described herein as "treated aluminium salt slag". This latter product is a preferred waste product.

The following Examples each show a composition which can be melted in a cupola furnace and the analysis of the composition and the fibres obtained from it.

Example 1

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8

100% briquettes consisting of :

9% cement

12% wool waste

22% ferro-chromium slag

5 23% shredder ash

29% diabase split

5% bauxite

resulting chemical composition (in wt. %) :

	SiO ₂	Al ₂ O ₃	TiO ₂	FeO	CaO	MgO	Na ₂ O	K ₂ O	Cr ₂ O ₃	CuO
10	41.8	20.5	1.2	6.1	14.8	11.8	1.5	1.0	1.4	0.12

Example 2

100% briquettes consisting of :

9% cement

5% converter slag

15 14% ferro-chromium slag

62% diabase split

10% aluminium dross (treated aluminium salt
slag)

resulting chemical composition (in wt. %) :

	SiO ₂	Al ₂ O ₃	TiO ₂	FeO	CaO	MgO	Na ₂ O	K ₂ O	Cr ₂ O ₃	ZnO
20	40.3	21.0	1.7	7.1	13.6	12.3	1.9	0.9	0.8	0.2

Example 3

45% diabase

55% briquettes consisting of :

25 9% cement

41% wool waste

23% ferro-chromium slag

14% EAF fly-ash

13% bottom ash from power plants

30 resulting chemical composition (in wt. %) :

	SiO ₂	Al ₂ O ₃	TiO ₂	FeO	CaO	MgO	Na ₂ O	K ₂ O	Cr ₂ O ₃	F ₂
	42.4	18.1	1.5	7.3	15.2	11.0	1.6	1.1	0.8	1.4

Example 4

Charge: 53% diabase + 22% ferro-chromium slag + 25%

35 cement briquette

Briquette composition: 14% Cement + 48% recycling material + 20% converter slag + 6% bottom ash from coal-fired power plant + 12% calcined bauxite

Resulting chemical composition (in wt.%):

5	SiO ₂	41.4
	Al ₂ O ₃	19.8
	TiO ₂	1.7
	FeO	7.4
	CaO	11.8
10	MgO	13.7
	Na ₂ O	1.7
	K ₂ O	0.8
	Viscosity (1400°C) = 18.6 Poise	
	Iron reduction is 30%	

15 Concentration of Cr: 1.6 wt.%

It is estimated that 10% of Cr from the charge is lost in tap iron and filter dust.

Example 5

20 In this Example the ferro-chromium slag is incorporated in the main furnace and a separate waste furnace is provided in which other materials are melted, as described in our corresponding application number....., filed today, reference PRL03828WO, and claiming priority from European application number 97309667.0.

25 Charge into cupola furnace:

3850 kg/h diabase

1050 kg/h slag from production of ferro-chromium alloy

With a loss on ignition of 4% this provides 0,96 (3850 + 1050) = 4700 kg of melt per hour from the cupola furnace.

30 In an electric waste melting furnace we charge:

900 kg/h mineral wool waste

50 kg/h aluminium dross from the secondary melting of aluminium (treated aluminium salt slag)

450 kg/h converter slag from production of steel

35 900 kg/h filter ash from the incineration of municipal solid waste

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The charge blend is melted continuously and mixed with the melt coming from the cupola furnace. The melt blend is poured onto a cascade spinner to form mineral fibres of the following chemical composition:

5	SiO ₂	41.1 %
	Al ₂ O ₃	20.0 %
	TiO ₂	1.7 %
	FeO	7.3 %
	CaO	12.9 %
10	MgO	12.6 %
	NaO ₂	2.1 %
	K ₂ O	1.2 %
	F+C ₁	0.5 %
	Others:	0.6 %

15 Both aluminium dross and the fly ash from the waste incineration contain considerable amounts of toxic components fluorine, chlorine, zinc and lead. The combined input is:

20		Charged Amount (Kg/h)	F (kg/h)	Cl (kg/h)	Pb (kg/h)	Zn (kg/h)
	Diabase	3850	-	-	-	-
	Ferro-chromium slag	1050	-	-	-	-
25	Production waste	630	2	-	-	-
	Aluminium dross	525	12	2	2	2
	Converter slag	315	4	-	-	-
	MSW fly ash	630	1	50	5	16
30	TOTAL	7000	19	52	7	18

30 By confirming this input to the separate waste melting furnace the effluence of fluorine, chlorine, zinc, lead and other volatile components to the flue gas and the filters is minimised.

35

CLAIMS

1. A process of producing man-made vitreous fibres having a content of at least 14% aluminium, measured as weight % Al_2O_3 , comprising
 - 5 providing a charge of raw mineral material in a furnace,
melting the charge in the furnace to form a melt
and fiberising the melt to form fibres,
characterised in that the charge comprises ferro-
10 chromium slag.
2. A process according to claim 1 in which the content of ferro-chromium slag in the charge is at least 10%, by weight based on total charge.
3. A process according to claim 1 or claim 2 in which the
15 furnace is a shaft furnace and the charge is a stack of solid mineral material.
4. A process according to claim 3 in which the furnace is a cupola furnace.
5. A process according to any preceding claim in which
20 the ferro-chromium slag has a content of aluminium of from 22 to 35%, content of iron from 1 to 10% and content of chromium of from 4 to 15%, all calculated by weight based on oxides.
6. A process according to any preceding claim in which
25 the fibres have a content of chromium of from 0.6 to 2 wt.%, measured as Cr_2O_3 based on oxides.
7. A process according to any preceding claim in which the fibres have a content of calcium of at least 8 wt.%, measured as CaO based on oxides.
- 30 8. A process according to any preceding claim in which the fibres have a content of magnesium of not more than 15 wt.%, measured as MgO based on oxides.
9. A process according to any preceding claim in which
35 the fibres have a content of iron of at least 2 wt.%, measured as FeO based on oxides.

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10. A process according to any preceding claim in which the fibres have a content of sodium and potassium of at least 1 wt.%, measured as $\text{Na}_2\text{O} + \text{K}_2\text{O}$ based on oxides.
- 5 11. A process according to any preceding claim in which the ferro-chromium slag is added to the furnace in solid form.
12. A process according to any preceding claim in which the ferro-chromium slag is incorporated in bonded briquettes which are added to the furnace.
- 10 13. A process according to any of claims 1 to 11 in which the ferro-chromium slag is incorporated in the charge as coarse lumps which are added directly to the furnace.
14. A process according to any preceding claim in which the fibres are formed into an insulation product.

AMENDED SHEET