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(54) Title: MANUFACTURE OF FOAM GLASS

(57) Abstract

Foam glass is manufactured from a molten glass composition which contains at least 0.2 % by weight of FeO and sufficient sulphur to satisfy the Fe^{++} ion and which has a negative redox value of at least -7 by contacting the molten glass composition with a refractory carbide, nitride or oxynitride capable of acting as a catalyst to produce sulphur dioxide with precipitation of iron. Silicon carbide and silicon oxynitride are preferred materials. The molten glass composition may be stirred using a rod which is 70 % silicon carbide and 30 % silicon nitride or silicon carbide may be sprinkled on the molten glass composition in a furnace. Alternatively, the molten glass composition may be poured from a glass melting furnace over a forehearth of silicon carbide. Precipitated iron and any other metal present are recovered as a by-product of the production of foam glass.

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MANUFACTURE OF FOAM GLASS

This invention relates to a method of manufacturing foam glass.

Foam glass having a bulk density of approximately 0.2 and a relatively high mechanical strength is known as a good inorganic insulating material. The currently used methods of manufacturing foam glass employ activated carbon and produce a foam glass of an unattractive black appearance. The foam glass product also tends to be expensive.

According to the present invention there is provided a method of manufacturing foam glass which includes the step of contacting a molten glass composition which contains at least 0.2% by weight of FeO and sufficient sulphur to satisfy the Fe^{++} ion, and which has a negative redox value of at least -7, with a carbide or nitride or oxynitride.

The preferred material for contacting the molten glass composition is silicon carbide. It is already well known that the presence of small errant pieces of silicon carbide left over from "dressing" of aluminous refractory blocks during construction of a glass melting furnace will cause bubble in glass produced in that furnace. The pieces of silicon carbide appear to have indefinite life and the production of glass is ruined by the bubble appearance with the result that furnaces

have had to be shut down while the pieces of silicon carbide are removed.

The present invention is based on the realisation that this property of silicon carbide may be utilized with an appropriate molten glass composition to produce violent bubble and a foam glass. Silicon oxynitride and commercially available silicon nitride, which contains the oxynitride as impurity, also have the same property, as do the carbides, nitrides and oxynitrides of other elements such as calcium and tungsten.

The glass compositions used in the process of the present invention are glass compositions which will give amber colouration. The amber colouration is produced by complex ions of iron oxide (FeO) and sulphur compounds, and it is thought that the process of the present invention proceeds as a result of the catalytic action of the carbide or oxynitride causing these complex ions to disintegrate with the sulphur ions taking up oxygen from the iron, and other metals more easily reduced than iron, thus releasing the metal, which is precipitated, and sulphur dioxide which is produced in large volume and foams the glass. At a temperature of 1500°C, 0.3% of SO_3 ion produces 5.4 cubic metres of gas per tonne of glass, each tonne of glass having a volume of 0.4 cubic metres.

Because the process of manufacturing foam glass in accordance with the present invention causes the precipitation of the iron or other metal, the process

has application in the treatment of industrial slags, particularly steel slags in order to recover the metal, usually iron, which would otherwise be wasted. In these circumstances the commercial emphasis may be on the recovery of the metal with the formation of the foam glass as a useful by-product.

According to this aspect of the present invention therefore there is provided a method of recovering iron from a slag containing at least 10% by weight of Fe_2O_3 comprising the steps of adjusting the redox to a negative value of at least -7, adding sulphate to the slag, if necessary, to produce a vitreous slag having sufficient sulphur to satisfy the Fe^{++} ion, contacting the vitreous slag with a carbide or nitride or oxynitride whereby a foam glass is formed with precipitation of iron, and recovering the precipitated iron.

The process of the present invention may conveniently be carried out by dropping the molten glass composition or vitreous slag over a weir into a holding pot or crucible where it is stirred by a silicon carbide silicon nitride rod. The foam glass is taken off by a platinum or other forehearth to machines where the foam glass may be moulded, blown, pressed, spun or simply dropped into water to provide a multiplicity of products. When the foam glass product is pressed, the density of the final product can be varied depending on the mould size, the volume of foam and the depth to which

a press is moved into the mould.

As an alternative to stirring the molten glass composition or vitreous slag with a silicon carbide/nitride rod, the molten glass composition or vitreous slag may be passed over a forehearth or down a spout made of silicon carbide, silicon nitride, silicon oxynitride, or other refractory carbide, nitride or oxynitride.

As a further alternative, the present invention may be performed by sprinkling an appropriate carbide, nitride or oxynitride, preferably silicon carbide or silicon oxynitride, in powder form on the molten glass composition or vitreous slag in the furnace. Foam glass will then be obtained as the output from the furnace.

The present invention will be further understood from the following examples of preferred methods in accordance therewith.

Example 1

Equal quantities by weight of a fly ash from a coal fired power station (P.F.A.) and of limestone were melted together in a crucible at a temperature of 1500°C for eight hours. A very dark amber coloured glass was produced and was found to contain approximately 1% by weight of Fe_2O_3. This molten glass was stirred with a rod consisting of 70% silicon carbide and 30% silicon nitride. The glass foamed so much that the density

was reduced to less than 0.2 gms/cc. Analysis of the foam glass showed that the iron content (Fe_2O_3) had been reduced to less than 0.04% and the foam glass obtained was colourless.

An alloy of iron and chromium (picked up from the refractories) was found on the base of the crucible. The rod of silicon carbide and silicon nitride was unaffected by the reaction which took place in the crucible.

Analysis of the fly ash used in this process showed that the fly ash contained sulphate and carbon and gave an 8% loss on ignition. The quantities of sulphate and carbon present were therefore such as to produce a high negative redox in the dark amber glass.

Example 2

66kg of calcium sulphate and 30kg of carbon were added to 1 tonne of steel slag containing a high iron oxide concentration (approximately 20% by weight Fe_2O_3) and stirred in with a silicon carbide/silicon nitride rod. A white foam glass was obtained with precipitation of iron which was recovered as metal. The white foam glass was suitable for use as a cement.

Foam glass products obtained by methods in accordance with the present invention may be used as building blocks for heat, sound or fire protection, for insulation purposes at high or low temperature, or as a refractory material.

In the preferred process in accordance with the present invention the raw materials used are waste matter from industrial processes which are cheap, and the present invention therefore provides foam glass at a low price compared with the foam glass currently available. Furthermore the foam glass is white or colourless and has a more pleasing appearance than the foam glass which is currently available.

CLAIMS:

1. A method of manufacturing foam glass which includes the step of contacting a molten glass composition which contains at least 0.2% by weight of FeO and sufficient sulphur to satisfy the Fe^{++} ion, and which has a negative redox value of at least -7, with a carbide or nitride or oxynitride.

2. A method according to Claim 1 wherein the molten glass composition is contacted with silicon carbide.

3. A method according to Claim 1 or Claim 2 wherein the molten glass composition is stirred with a rod comprising, by weight, 70% silicon carbide and 30% silicon nitride.

4. A method according to Claim 1 or Claim 2 wherein the molten glass composition is caused to pass over a portion of a furnace constructed from silicon carbide.

5. A method according to Claim 4 wherein the portion of the said furnace is constructed from a material consisting of, by weight, 70% silicon carbide, 30% silicon nitride.

6. A method according to Claim 1 or Claim 2 wherein silicon carbide in powder form is sprinkled on the surface of the molten glass composition.

7. A method according to any one of the preceding claims wherein the molten glass composition is a vitreous slag.

8. A method according to Claim 7 wherein the vitreous slag is formed by adding sulphate to an industrial or domestic slag.

9. A method according to Claim 7 wherein the vitreous slag is formed by adding sulphate and carbon to a steel slag.

10. A method according to any one of Claims 1 to 7 wherein the molten glass composition is formed by heating fly ash with an equivalent quantity of limestone at 1500°C.

11. A method of recovering iron from an industrial waste material by a method according to any one of the preceding claims and including the further step of recovering precipitated iron.

12. A method of recovering iron from a slag containing at least 10% by weight of Fe_2O_3 comprising the steps

of adjusting the redox to a negative value of at least -7, adding sulphate to the slag, if necessary, to produce a vitreous slag having sufficient sulphur to satisfy the Fe^{++} ion, contacting the vitreous slag with a carbide or nitride or oxynitride whereby a foam glass is formed with precipitation of iron, and recovering the precipitated iron.

INTERNATIONAL SEARCH REPORT

International Application No PCT/GB 90/00145

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC5: C 03 C 11/00, C 04 B 5/06, C 21 B 3/06

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
IPC5	C 03 B; C 03 C; C 04 B; C 21 B

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category *	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
X	EP, A1, 0242872 (PIEPER, HELMUT) 28 October 1987, see page 5, line 21 - line 25; abstract	1
A	GB, A, 1392724 (THE CARBORUNDUM COMPANY) 30 April 1975, see the whole document	1-10
A	GB, A, 1442854 (EUROC ADMINISTRATION AB) 14 July 1976, see the whole document	1-10

* Special categories of cited documents: [10]

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IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
20th April 1990	03. 05. 90
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III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
A	Derwent's abstract No. 435 99 B/23, SU 618 352, publ. week 7923	1-10
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A	US, A, 3126274 (RICHARD O. AAMOT ET AL) 24 March 1964, see the whole document	11-12
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ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO. PCT/GB 90/00145

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This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 28/02/90
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Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A1- 0242872	28/10/87	DE-A-	3616110	05/11/87
		DE-A-C-	3700382	21/07/88
GB-A- 1392724	30/04/75	CA-A-	965929	15/04/75
		DE-A-	2220238	09/11/72
GB-A- 1442854	14/07/76	CA-A-	1001665	14/12/76
		DE-A-	2335146	24/01/74
		FR-A-B-	2192986	15/02/74
		SE-B-	364699	04/03/74
		US-A-	3942990	09/03/76
US-A- 3126274	24/03/64	NONE		

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