Title: BUILDING PRODUCT MATERIAL AND METHOD FOR MAKING IT

Abstract: A method of making a building product material from hazardous recycled Cathode Ray Tube glasses. The method comprising mixing particulate recycled Cathode Ray tube and container glasses with a sodium silicate binder, pressing the mixture to form a compact, introducing carbon dioxide gas to cure the binder immediately following pressing, and subsequently firing the compact.

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BUILDING PRODUCT MATERIAL AND METHOD FOR MAKING IT

This invention concerns a method of converting hazardous recycled glass into safe building products, by a method of making a building product material from such glasses, such a material, a method of making an article from such a building product material, and such an article. In particular, the invention relates to the conversion of Cathode Ray Tube (CRT) glasses.

A significant amount of waste glasses from discarded cathode ray tubes are available for recycling, but appropriate uses for this are not readily identifiable, particularly due to their hazardous nature related to high Lead, Barium and Strontium content of such glasses, and concerns regarding such metals entering the environment in solution as a leachate sourced from the CRT glasses.

There are two CRT glass types contained in a cathode ray tube, these are the CRT funnel (or cone) which contains Lead, and the CRT panel which contains Barium and Strontium.

Significant amounts of other types of waste glass are available and are currently being recycled.

All percentages given in this specification are by weight.

According to the present invention there is provided a method of making a building product material, the method comprising the steps of:

blending specific proportions, size ranges and CRT and non-CRT glass types with an inorganic binder to produce a product material, forming a compact of a product material;

and firing the compact.
Specific proportions, size ranges and glass types are used, to enable mechanisms which encapsulate and/or dilute the CRT glasses in the building product. This significantly reduces the metal leaching potential of the CRT glasses.

The major mechanism contributing to the reduction in leachate potential in the encapsulation technique involves the coating and permanently bonding of fine container glass particles to the surface of relatively larger CRT glass grains. This significantly reduces the exposed reaction surface of the CRT grains. There is also a minor mechanism of dilution involved, reducing the leachate potential in proportion to the reduction of the proportion of coarse CRT glass present by substitution with fine container glass.

There are two dilution types, characterised by the particle size ranges involved, but the major and minor mechanisms contributing to the reduction in leachate potential in both types is identical. The major mechanism contributing to the reduction in leachate potential in the dilution technique is the reduction in the proportion of CRT glass present by substitution with container glass. The minor mechanism contributing to the reduction in leachate potential is some encapsulation activity, as described in the previous paragraph.

The present invention covers a method of manufacturing a building product utilising both the encapsulation technique and the dilution technique.

The product material preferably includes greater than 97% recycled glasses.

The cathode ray tube may be physically separated into two glass components: panel glass (containing Barium and Strontium) and funnel glass (containing Lead).

CRT panel glass alone or a mixture of CRT panel and funnel glass may be used as a product material component.

The recycled glass may be colour sorted.
The hazardous recycled glass may be obtained from glasses used in cathode ray tubes, from such as computer monitors or televisions; the non-hazardous recycled glass may be obtained from container glass, such as bottles or jars.

The product material may comprise a mixture of one or more different types of recycled glass.

The recycled glass in the product material may have a particle size of less than 2000μm.

For the encapsulated technique, the CRT glass may be processed such that the particle size ranges between 100μm to 2000μm. For an embodiment of the diluted technique, the CRT glass may be processed such that particle size is less than 300μm.

For an alternative embodiment of the diluted technique, the CRT glass may be processed such that the particle size is less than 100μm.

The container glass component may have a particle size range of less than 75μm for the encapsulated technique or less than 2000μm for the diluted techniques.

The recycled glass may be crushed prior to formation of the compact. The recycled glass may be primary milled following crushing. The recycled glass may be secondary milled following primary milling.

The oversize particles are removed from the crushed and milled bulk glasses using vibratory screening. The less than 100μm CRT glass particles and less than 75μm container glass particles may be removed from their respective crushed and milled bulks by air classification techniques.

Contaminants are preferably removed during and/or after crushing and/or milling.
The recycled glass may be coloured, and may be coloured by the addition of a colouring material which may be in the form of metallic oxides, pigments, or stains.

The colouring material is preferably mixed with the glass components after the mixing with the binder.

For the encapsulated technique, the 2000 to 100μm CRT glass component is preferably firstly mixed with the inorganic binder, after which the less than 75μm container glass component is preferably added and mixed.

For an embodiment of the diluted technique, the less than 2000μm CRT glass component is preferably blended with the less than 2000μm container glass component, then is preferably mixed with inorganic binder.

For an alternative embodiment of the diluted technique, the less than 2000μm container glass component is preferably mixed with the inorganic binder, afterwards the less than 100μm CRT glass component is preferably added and mixed.

The inorganic binder may be cured during or following formation of the compact but prior to firing.

The inorganic binder may comprise sodium silicate, desirably in liquid form. Preferably less than 3.5% inorganic binder is included, and desirably less than 2%. The sodium silicate may be cured by carbon dioxide gas. The carbon dioxide gas is desirably introduced at a pressure of between 1 and 4 Bar, and for a time period of between one and ten seconds. The pressing pressure is preferably in the range 15 to 62 Mpa.

The compact may be formed by pressing, vibropressing or ramming the product material in a mould space. The inorganic binder is preferably cured following pressing, vibropressing or ramming of the compact, but whilst the compact is still in the mould
space. A perforated punch, other permeable item, or inlet into the mould space, may be provided through which carbon dioxide is passed to enter the compact.

One or more surfaces of the compact may be profiled. This may be achieved by using any of a profiled punch, a profiled mould, or a profiled former provided in the mould space. Alternatively or in addition, a surface of the compact can be treated prior to firing, and desirably by any of brushing, compressed air or glass blasting.

A different product material may be provided just near a surface of the compact, and this can be achieved by initially filling the mould space with the different material, or finally filling the mould space with the different material.

A surface of the compact may be decorated and this can be achieved by spraying, atomisation, brushing, and/or printing and in particular screen printing.

The compact can be finished following firing, and by any of edge grinding, surface grinding, surface polishing and/or cutting.

Material rejected during formation is preferably recycled in the method.

Firing preferably takes place at a peak temperature of between 600 and 725°C, with a peak temperature dwell of between five and sixty minutes.

The invention also provides a building product material made by a method according to any of the preceding paragraphs.

The invention further provides a method of making an article, the method comprising using a method according to any of said preceding paragraphs, with a mould space of a required shape to form the article.

The invention further provides an article made by such a method.
The article may comprise a building product, including any of interior/exterior bricks, pavers, blocks, cladding or garden ware.

Embodiments of the present invention will now be described by way of example only, and with reference to the figures of the accompanying drawings in which:

Fig. 1 is a cross-sectional view of a press; and
Fig. 2 is a cross-sectional view of a vibropress.

Two general examples relating to the formation of a compact by pressing and vibropressing will now be briefly described followed by specific examples.

**General example of pressing.**

A compact is formed by pressing a product material formed largely of particulate recycled glass. The compact is formed in the apparatus 10 shown in Fig. 1 of the accompanying drawing. The apparatus 10 includes a press table 12 which mounts a mould box 14 which defines a pressing space 16. A lower punch 18 is provided in the bottom of the space 16.

In use, product material 20 to be pressed is located in the space 16 above the lower punch 18. An upper punch 22 is located in the space 16 on the top of the material 20, and pressing takes place.

Following pressing, the upper punch 22 is raised to the position shown in the drawing and an inflating seal 24 which extends around the perimeter of the upper punch 22 and in this position remains in the space 16, is inflated. An accelerant which in this instance is carbon dioxide to cure the inorganic binder in the product material 20, is introduced from a supply 26 through a channel 28 into the mould space 16. A sealing valve 30 is provided over the opening of the channel 28 leading into the space 16, to prevent product material entering the channel 28.
After a required exposure time to the accelerant gas, injection of the gas is stopped and the seal 24 is deflated. The upper punch 22 is then fully withdrawn from the mould box and the hardened product is ejected from the mould box by the lower punch 18. The inflating seal 24 around the upper punch 22 ensures that the accelerant gas is retained in the mould space 16.

The product material is pressed to a specific pressure depending on the material recipe and type. The material includes a binder which in all of the following examples is sodium silicate in liquid form. The binder is cured by exposing the pressed material to carbon dioxide at specified pressures and time duration, prior to removal from the mould space. The pressure and duration of exposure to carbon dioxide gas depends on the thickness of the material and the material permeability.

The green compact following removal from the mould space 16 is subsequently fired at required parameters for the material. Any reject compacts at any point are returned for recycling in the process.

**General example of Vibropressing.**

A compact is formed by vibropressing a product material formed largely of particulate recycled glass, in a similar manner to that described for pressing. However, in addition to the example of pressing, extra components are included in the apparatus to facilitate vibration of upper punch, lower punch and so the product material. The inclusion of vibration during pressing facilitates compaction to the required bulk density at lower applied pressure. The compact is formed in the apparatus, generally designated 32, shown in Fig. 2 of the accompanying drawings. The apparatus 32 includes a press table 12 to which is mounted a mould box 14 which defines a pressing space 16. A lower punch 18 is provided in the bottom of the space 16. The lower punch 18 is supported above the press table 12 lower isolating tubes 34. Lower load transfer pillars 36 are located internally within the isolating tubes 34. Vibrating motors 38 are positioned on the underside of the lower punch 18. An upper punch 22 is supported below an adaptor plate 40, by isolating tubes 34, within which are located upper load
transfer pillars 36. Vibrating motors 38 are positioned on the topside of the upper punch 22.

In use, product material 20 to be pressed is located in the space 16 above the lower punch 18. The upper punch 22 is located in the space 16 on the top of the material 20, and the vibrating motors 38 are energised. The isolating tubes 34 ensure the vibration is restricted to the required area i.e. within the pressing space 16 and between the upper and lower punches 18, 22. A ram 42 provided above the adapter plate 40 is slowly extended and begins to compact the product material, while the vibration encourages more efficient grain and particle packing. When the load transfer pillars 36 make solid contact and accept load, the vibrating motors 38 are de-energised. Full load pressing then takes place.

Following pressing, the upper punch 22 is raised to the position shown in the drawing and an inflatable seal 24 which extends around the perimeter of the upper punch 22 and which in the position shown, remains in the space 16, is inflated. A binder curing accelerant, for example carbon dioxide, is introduced from a supply 26 through a channel 28 into the mould space 16. A sealing valve 30 is provided over the opening of the channel 28 leading into the space 16, to prevent product material entering the channel 28.

After a required exposure time to the accelerant gas, injection of the gas is stopped and the seal 24 is deflated. The upper punch 22 is then fully withdrawn from the mould box and the hardened product is ejected from the mould box by the lower punch 18. The inflating seal 24 around the upper punch 22 ensures that the accelerant gas is retained in the mould space 16.

The product material is pressed to a specific pressure depending on the material recipe and type. The material includes a binder which in all of the following examples is sodium silicate in liquid form. The binder is cured by exposing the pressed material to carbon dioxide at specified pressures and time duration, prior to removal from the
mould space. The pressure and duration of exposure to carbon dioxide gas depends on the thickness of the material and the material permeability.

Following removal from the mould space 16, the green compact is subsequently fired at required parameters for the material. Any reject compacts at any point are returned for recycling in the process.

The product material for pressing in either of the manners described above is initially prepared as follows. The glass is coarsely crushed. Contaminants may be removed after the coarse crushing operation. The glass is then primary milled and contaminants again may be removed. The glass is then secondary milled and then passed through a series of vibrating screens to provide fractions of required sizes. Oversize glass is returned to secondary milling. When required, the milled and screened CRT glass is passed through an air classifier to separate the less than 100μm fraction from the bulk.

Example One

The following example relates to the aforementioned encapsulated technique where fine container glass particles are bonded to the surface of relatively larger CRT glass openings.

90% cathode ray tube panel glass with a particle size range of less than 2000μm and greater than 100μm mixed with +2% liquid sodium silicate; then 10% mixed colour container glass with a particle size range of less than 75μm was mixed in to the batch.

The product material was pressed at a pressure of 30.9MPa in the press apparatus 10 described with reference to Fig. 1 to a thickness of 65mm. Carbon dioxide gas was fed into the space 16 following pressing at 2 Bar pressure for 5 seconds.

The hardened compact was ejected from the space 16 and fired at a rate of 30°C per minute to an interim temperature of 620°C for a dwell of 60 minutes, then fired at a rate of 30°C per minute to a peak temperature of 640°C for a dwell of 60 minutes, and a subsequent average cooling rate of 2°C per minute.
This produced a material with the appearance of a speckled grey/green brick which had water absorption of 9% and a compressive strength of 65 N/mm². A sample of the product was crushed to less than 2mm and subjected to a severe exposure regime of the following: hot concentrated nitric acid, hot 30% solution hydrogen peroxide and hot concentrated hydrochloric acid. The leachate was analysed using Inductively Coupled Plasma.

Analysis of the leachate yielded the following results:

Strontium less than 0.38 ppm; Barium less than 0.47 ppm.

**Example Two**

The following example relates to the dilution technique where the reduction in leachate potential is realised by substitution of CRT glass with container glass.

85% colour blended container glass with a particle size range of less than 2000µm was mixed with +2% liquid sodium silicate; then 15% cathode ray tube panel glass with a particle size range of less than 100µm was mixed in to the batch; the mixture was then pressed at a pressure of 45MPa in the apparatus 10 described with referenced to Fig. 1 to a thickness of 50mm and carbon dioxide gas was fed into the space 16 under similar conditions as for example one.

The hardened compact was ejected from the space 16 and fired at a rate of 30°C per minute to an interim temperature of 650°C for a dwell of 60 minutes, then fired at a rate of 30°C per minute to a peak temperature of 670°C for a dwell of 60 minutes, and a subsequent average cooling rate of 3°C per minute.

This produced a material with the appearance of a green paver which had water absorption of 10% and a transverse strength of 9.5 Mpa.

**Example Three**
A further example of the dilution technique

50% cathode ray tube panel glass with a particle size range of less than 2000μm, was blended with 50% brown colour sorted container glass, and then mixed with +2% liquid sodium silicate. The product material was pressed at a pressure of 45MPa in the apparatus 10 described with reference to Fig. 1 to a thickness of 65mm. Carbon dioxide gas was fed into the space 16 following pressing at 2 Bar pressure for 5 seconds.

The hardened compact was ejected from the space 16 and fired at a rate of 30°C per minute to an interim temperature of 640°C for a dwell of 60 minutes, then fired at a rate of 30°C per minute to a peak temperature of 650°C for a dwell of 60 minutes, and a subsequent average cooling rate of 3°C per minute.

This produced a material with the appearance of a speckled yellowish brown paver which had water absorption of 11% and a transverse strength of 8.7 Mpa.

Analysis of the leachate (test method as described in example One) yielded the following results:

Strontium less than 0.85 ppm; Barium less than 0.91 ppm.

Example Four

A further example of the encapsulation technique

80% cathode ray tube panel glass with a particle size range of less than 2000μm and greater than 100μm was mixed with +2% liquid sodium silicate; then 20% brown colour sorted container glass with a particle size range of less than 75μm was mixed in to the batch. The product material was vibropressed at a pressure of 15.4MPa in the apparatus 32 described with reference to Fig. 2 to a thickness of 25mm. Carbon dioxide gas was fed into the space 16 following pressing at 2 Bar pressure for 5 seconds.
The hardened compact was ejected from the space 16 and fired at a rate of 30°C per minute to an interim temperature of 630°C for a dwell of 15 minutes, then fired at a rate of 30°C per minute to a peak temperature of 650°C for a dwell of 30 minutes, and a subsequent average cooling rate of 4°C per minute.

This produced a material with the appearance of a specked brown 300mm cladding tile which had water absorption of 8.2% and a transverse strength of 15.1 MPa. The material obtained was surface ground to reveal a fine yellow and off-white texture.

There are thus described methods, and materials produced by such methods, providing a wide range of uses for recycled CRT glasses and container glass.

This process provides a novel method for converting hazardous recycled CRT glasses into safe commercial building products.

The process is intentionally designed to convert hazardous CRT glasses into a form facilitating a safe and useful function in the built environment.

The process intentionally uses solely glass(es) as the principal product structural material to:

i) reduce the amount of binder required, because the glass is non-absorbent;
ii) permit firing the product at a low temperature, because glasses begin to soften at relatively low temperature;
iii) permit rapid heating of the product during firing, because the glass does not exhibit endothermic reactions during heating (which introduce thermal barriers to heat transfer);
iv) reduce the energy required to raise the temperature of the product during firing, because glasses possess relatively low specific heat capacity and no endothermic reactions;

The CRT glass raw material is intentionally milled to a relatively coarse size to:
i) reduce the exposed reaction surface area;
ii) increase the size differential between the CRT grains and the container glass it is subsequently mixed with;
iii) reduce milling energy consumption;
iv) reduce wear on components of the milling equipment;
v) reduce the binder component requirement, by minimizing the surface area of the milled glass;
vi) produce the required texture and pore size, promoting durability in the final product.

The products are intentionally compacted and then gassed under pressure whilst still in the press, to:
i) reduce the magnitude of shrinkage during firing, though elimination of porosity during pressing;
ii) reduce the maturing temperature and increase final strength, through elimination of porosity during pressing;
iii) reduce the binder requirement, by increasing intimacy of particle contact;
iv) simplify the hardening process, by facilitating gassing through existing standard press components;
v) allow the rapid hardening of the product before removal from the mould box, to increase press production output.

The products may be intentionally vibrated during the initial stages of compaction to:
i) improve the efficiency of grain and particle packing within the product material;
ii) reduce the applied load required to achieve the desired bulk density in the pressed product, facilitating the production of larger surface area products without a requirement for increased press loading capacity.

A process which can totally recycle 100% of its own final product and product from any stage of the process, as its own glass feedstock.
The use of the inorganic sodium silicate binder provides a number of advantages. Firstly, relatively small proportions of this material are required, and this is a non volatile material which can thus be handled without the requirement for fume extraction and the like. During firing the sodium silicate is incorporated into the material. Therefore this binder and also the materials which have also already been fired at a higher temperature, produce very few emissions during firing. The sodium silicate once cured by carbon dioxide provides sufficient rigidity to the materials to be handled up to and during firing. The low proportions of sodium silicate mean that the materials can be fired immediately following pressing without any requirement for drying or other processing.

The materials formed can be readily pressed into required shapes to make products such as interior or exterior bricks, pavers, blocks, cladding products, or garden ware.

Various other modifications may be made without departing from the scope of the invention. For example other materials and parameters or a mixture of those described above can be used. The surface of the compact can be coloured prior to firing by the application of a suitable colourant using for example conventional techniques of spraying, atomisation, brushing or printing etc., and particularly screen printing. It is to be realised that reject material or product can at any time be recycled in the process. If required the surface of the compact can be processed prior to firing by brushing, compressed air or glass blasting, with any removed material being returned into the process. Following firing the material can be finished by edge or surface grinding, surface polishing or cutting.

Whilst endeavouring in the foregoing specification to draw attention to those features of the invention believed to be of particular importance it should be understood that the Applicant claims protection in respect of any patentable feature or combination of features hereinbefore referred to and/or shown in the drawings whether or not particular emphasis has been placed thereon.
1. A method of converting recycled Cathode Ray Tube glasses into a building product, by a method of making a building product material, the method including the steps of:
forming a compact of a product material, the product material including particulate recycled CRT glasses, particulate recycled container glass and an inorganic binder; and firing the compact.

2. A method according to claim 1, characterised in that the recycled CRT glasses are rendered safe in the building product by being encapsulated by, and/or diluted by the recycled container glass.

3. A method according to claim 2, characterised in that the product material includes greater than 70% by weight of CRT glasses in the encapsulated type building product.

4. A method according to claim 2 or claim 3, characterised in that the product material includes less than 30% by weight of container glass in the encapsulated type building product.

5. A method according to any of claims 2 to 4, characterised in that the recycled CRT glasses in the product material in the encapsulated type building product, have a particle size of less than 2000μm and greater than 100μm.

6. A method according to any of claims 2 to 5, characterised in that the recycled container glass in the product material has a particle size of less than 75μm in the encapsulated type building product.

7. A method according to claim 2, characterised in that the product material includes less than 70% by weight of CRT glasses in the diluted type building product.
8. A method according to claim 7, characterised in that the product material and greater than 30% by weight of container glass in the diluted type building product.

9. A method according to claim 7 or claim 8, characterised in that the recycled CRT glasses in the product material in the diluted type building product, have a particle size of less than 2000µm.

10. A method according to claim 7 or claim 8, characterised in that the recycled CRT glasses in the product material in the diluted type building product, have a particle size of less than 100µm.

11. A method according to any of claims 7 to 10, characterised in that the recycled container glass in the product material has a particle size of less than 2000µm in the diluted type building product.

12. A method according to any preceding claim, characterised in that the product material includes greater than 97% by weight of recycled glasses.

13. A method according to any preceding claim, characterised in that the container glass is colour sorted.

14. A method according to any preceding claim, characterised in that: the recycled CRT glass is obtained from glasses used in cathode ray tubes, from such as computer monitors or televisions; the non-hazardous recycled container glass is obtained from such as bottles or jars.

15. A method according to claim 14, characterised in that the product material includes a mixture of one or more different types of recycled glass.

16. A method according to any of the preceding claims, characterised in that the recycled glass is crushed prior to formation of the compact.
17. A method according to claim 16, characterised in that the recycled glass is milled following crushing.

18. A method according to claims 16 or 17, characterised in that contaminants are removed during and/or after crushing and/or milling.

19. A method according to any of claims 16 to 18 characterised in that less than 100μm CRT glass particles and less than 75μm container glass particles are removed from their crushed and milled bulk, by air classification techniques.

20. A method according to any of the preceding claims, characterised in that the recycled glass is coloured by the addition of a colouring material which is in the form of metallic oxides, pigments, or stains.

21. A method according to claim 20, characterised in that the recycled glass is mixed with the colouring material prior to formation of the compact.

22. A method according to any of the preceding claims, characterised in that the inorganic binder is cured during or following formation of the compact but prior to firing.

23. A method according to any of the preceding claims, characterised in that the inorganic binder comprises sodium silicate.

24. A method according to claim 23, characterised in that the sodium silicate is in liquid form.

25. A method according to claims 23 or 24, characterised in that the sodium silicate is cured by carbon dioxide gas.

26. A method according to claim 25, characterised in that the carbon dioxide gas is introduced at a pressure of between 1 and 4 bar.
27. A method according to claims 25 or 26 characterised in that the carbon dioxide gas is introduced for a time period of between one and twenty seconds.

28. A method according to any of the preceding claims, characterised in that less than 3.5% inorganic binder is included.

29. A method according to claim 28, characterised in that less than 2.5% inorganic binder is included.

30. A method according to any of the preceding claims, characterised in that the pressing pressure to form the compact is in the range 15 to 62 MPa.

31. A method according to any of the preceding claims, characterised in that the compact is formed by pressing the product material in a mould space.

32. A method according to any of the preceding claims, characterised in that the compact is formed by vibropressing the product material in a mould space.

33. A method according to claims 31 or 32 characterised in that the inorganic binder is cured following pressing or vibropressing of the compact, but whilst the compact is still in the mould space.

34. A method according to claim 25 or any of claims 26 to 33 when dependent on claim 22, characterised in that a perforated punch, other permeable item, or inlet into the mould space, is provided through which carbon dioxide is passed to enter the compact.

35. A method according to any of the preceding claims, characterised in that one or more surfaces of the compact are profiled.
36. A method according to claim 35 when dependent on claim 31 or 32 characterised in that the compact is profiled by using any of, a profiled punch, a profiled mould, or a profiled former provided in the mould space.

37. A method according to any of the preceding claims, characterised in that a surface of the compact is treated prior to firing by any of brushing, compressed air or glass blasting.

38. A method according to claim 31 or claim 32, or any of claims 33 to 37 when dependent on claims 31 or 32, characterised in that a different material is provided just near a surface of the compact by finally filling the mould space with the different material.

39. A method according to claim 31 or claim 32, or any of claims 33 to 38 when dependent on claims 31 or claim 32, characterised in that a different material is provided just near a surface of the compact by initially filling the mould space with the different material.

40. A method according to any of the preceding claims, characterised in that a surface of the compact is decorated.

41. A method according to claim 40, characterised in that the decoration is achieved by spraying, atomisation, brushing, and/or printing and in particular screen printing.

42. A method according to any of the preceding claims, characterised in that the compact is finished following firing by any of edge grinding, surface grinding, surface polishing and/or cutting.

43. A method according to any of the preceding claims, characterised in that product material rejected during formation is recycled in the method.
44. A method according to any of the preceding claims, characterised in that firing takes place at a peak temperature of less than 725°C.

45. A method according to any of the preceding claims, characterised in that firing takes place at a peak temperature dwell of between five and sixty minutes.

46. A building product material made by a method according to any of the preceding claims.

47. A method of making an article, the method comprising using a method according to any of claims 1 to 46 with a mould space of a required shape to form the article.

48. An article made by the method of claim 47.

49. An article as claimed in claim 48 characterised in that the article comprises a building product including any of interior/exterior bricks, pavers, blocks, cladding or garden ware.
**INTERNATIONAL SEARCH REPORT**

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC 7 C04B14/22 C03C14/00

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C04B C03C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

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<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
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<td>WO 2004/050578 A (STAFFORDSHIRE UNIVERSITY; READ, DAVID; JOSEPH; ANDERSON, MICHAEL; DOWL) 17 June 2004 (2004-06-17)</td>
<td>1,2,5-49</td>
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<td>A</td>
<td>DE 44 33 795 A1 (ED. ZUEBLIN AG, 70567 STUTTGART, DE) 28 March 1996 (1996-03-28) the whole document</td>
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<td>A</td>
<td>FR 2 774 089 A (DEMONTEAGE VALORISATION ELECTRONIQUE - DEMOVALE) 30 July 1999 (1999-07-30) page 2, line 1 - page 3, line 13; tables I,II</td>
<td>1,46,48</td>
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Further documents are listed in the continuation of box C. Patent family members are listed in annex.

* Special categories of cited documents:

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- **Y** document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- **M** document member of the same patent family

Date of the actual completion of the international search

13 October 2005

Date of mailing of the international search report

20/10/2005

Name and mailing address of the ISA
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Authorized officer

Stroud, J
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<td>WO 00/44685 A (JIN, WEIHUA) 3 August 2000 (2000-08-03) page 2, line 13 - line 19 page 7, line 30 - page 8, line 16</td>
<td>1,46,48</td>
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<tr>
<td>Patent document cited in search report</td>
<td>Publication date</td>
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<tr>
<td>DE 4433795 A1</td>
<td>28-03-1996</td>
<td>NONE</td>
</tr>
<tr>
<td>FR 2774089 A</td>
<td>30-07-1999</td>
<td>NONE</td>
</tr>
<tr>
<td>FR 2774088 A</td>
<td>30-07-1999</td>
<td>NONE</td>
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<td>US 6296699 B1</td>
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