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(54) **Title**: METHOD FOR PRODUCING A SHAPE RETAINING MASS

(57) **Abstract**: A method of producing a shape retaining mass having a compressive strength, measured in accordance with the ASTM standard test method D 698-12, of at least 2 MPa, comprising the steps of: Step 1. mixing of a binder composition [composition (B), herein after] comprising at least one carbonating agent which is selected from the group consisting of potassium carbonate, potassium bicarbonate and magnesium carbonate hydroxide hydrate compounds of general formula (I): x Mg CO_3.y $Mg(OH)_2$.z H_2O wherein x is a number in the range of 3.5 – 4.5, y is a number in the range of 0.5 – 1.5, and z is a number in the range of 3.5 – 5.5, with at least a particulate steel slag material, thereby forming a mixture [mixture M, herein after] and wherein said particulate steel slag material is containing calcium silicate phases and at least chromium and is present in said mixture M in an amount of at least 50 % by dry weight (dry wt. %), relative to the total dry weight of the mixture M, and Step 2. hardening of the mixture M, as obtained in Step 1., in the presence of water, thereby producing the shape retaining mass.

"METHOD FOR PRODUCING A SHAPE RETAINING MASS"

FIELD OF INVENTION

The present invention relates to an environmentally friendly method of producing a shape retaining mass having a compressive strength of at least 2 MPa, in particular a basement material, including the use of steel slag particulate material. Said shape retaining mass has a considerably reduced leaching behaviour of the heavy metals which are contained in the steel slag particulate material.

BACKGROUND OF THE INVENTION

Steel slag materials are by-products which are generated during the production of steel.

Stainless steel slags, derived from the production of stainless steel are a particular group of slags. Stainless steel slags comprise mainly calcium oxide (CaO) and silicon dioxide (SiO_2). For the production of stainless steel, use is moreover additionally made of chromium and often also of nickel and/or of molybdenum.

Thus, the stainless steel slags contain considerable amounts of heavy metals, such as notably chromium and often also of nickel and/or of molybdenum, which are problematic in view of their leaching behaviour. According to some legislations, the dumping of these stainless steel slags as waste need to be carried out under controlled conditions.

In order to avoid the environmental-hygienical problems related to the dumping of these stainless steel slags as waste, attempts have already been made to develop methods of processing these stainless steel slags, i.e. methods for converting them into economically valuable materials which can be used in several fields of technology such as road

engineering, building engineering, construction and public works and soil stabilizations.

For example, in EP-B-0837043, EP-B-1055647 and in EP-B-1146022 the leaching problems of stainless steel slags can be solved by crushing the steel slags, removing the valuable stainless steel particles therefrom and by applying the different fractions of the remaining crushed slags in bounded applications. Specifically, the coarser fractions of the crushed stainless steel slag can be used in concrete or asphalt.

In the article "The use of stainless steel slag in concrete", A. Kortbaoui, A. Tagnit-Hamou, and P. C. Aïtcin, Cement-Based Materials, p. 77-90, 1993, a process for producing mortar or concrete was proposed comprising the step of mixing at least a fine fraction of steel slag particles, containing a significant amount of γ-dicalcium silicate, with at least a hydraulic binding agent and with water to produce said mortar or said concrete. However, the amount used was limited by the negative effect of that fine fraction on the workability of the cement mix. Since the fine steel slag fraction can absorb large quantities of water, using the normal amounts of water in the mixture will result in a thick, nearly solid paste. In particular, this negative impact on the workability of the cement mix would make it inadequate for use in self-compacting concrete, as defined by the European Guidelines for Self-Compacting Concrete, published by the European Precast Concrete Organisation, the European Cement Association, the European Ready-mix Concrete Organisation, the European Federation of Concrete Admixture Associations and the European Federation of Specialist Construction Chemicals and Concrete Systems. Adding more water, however, will have a negative impact on the strength of the concrete, since a water film forms around each steel slag particle which will leave a void once the concrete hardens. Attempts to compensate this by adding plasticizer or cement will increase the cost.

This being said, due to its higher gamma dicalcium silicate (γ-C2S) content, the very fine fraction of these crushed steel slags having a particle size of 0 - 0.5 mm has high water absorption properties and is thus not suited for being used as a filler/ fine aggregate in the manufacturing of a shape retaining mass, such as notably concrete or asphalt.

In practice, these fines are in general separated off from the coarser sand fraction (having a particle size larger than 0.5 mm) of the stainless steel slags by a wet separation technique.

In WO 2009/090219, these fines are aggregated into larger grains so as to form a coarser granular material. Subsequently said coarser granular materials are carbonated under a relatively low pressure by means of carbon dioxide so as to produce a carbonated granular material. By the combination of the aggregation step and the carbonation step, a material can be obtained with significantly lower water absorption and therefore a better workability when it is mixed with cement and water. The carbonation converts calcium and/or magnesium hydroxides into calcium and magnesium carbonate phases with binding properties that heal the microcracks in the fine steel slag particles, significantly reducing their water demand, and bind them together within each grain, providing thereby a harder, coarser material. The carbonated granular materials of WO 2009/090219 have the advantage that they can be manufactured in advance and stored so that they can be mixed with cement and water in a conventional manner. However, granulation and carbonation equipment is needed and the granulation and carbonation process is also time consuming and thereby relatively expensive. Moreover, the carbonation process cannot be carried out on-site, in order to produce basement layers, so that binder compositions are still required to produce the final product (concrete).

Another carbonation method for producing more valuable construction materials starting from the fines of crushed stainless steel

slags which have a size of between 0 and 0.5 mm is disclosed in WO-A-2009/133120. In this method the fines are first press-moulded with a relatively high compaction pressure of between 5 and 65 MPa, and the obtained compact is subsequently carbonated under a relatively high temperature and pressure. In this way, instead of granulates larger carbonated compacts with a relatively high compressive strength can be produced. By controlling the porosity and the intrinsic permeability of the compacts, and by carbonating for several hours (more particularly for 18 hours at an increased pressure and temperature), compressive strengths of between 26 and 66 MPa were obtained with a 0 – 500 µm fine stainless steel slag fraction which was press-moulded with a compaction pressure of 182 kg/cm² (= 17.8 MPa). A drawback of this prior art method is that, notwithstanding the fact that relatively small blocks were carbonated (62x62x32 mm and 120x55x46 mm), high gas pressures were required which makes the process quite costly, and which cannot be applied on-site in order to produce stiff basement layers.

In other words, in all of these processes gaseous CO_2 is used for the carbonation process which cannot be introduced in larger volumes such as basement layers, or is at least difficult to be introduced, so that notwithstanding the fact that a shaping and carbonation step has already been carried out, a binder is still needed to produce the final product.

EP 2 160 367 describes the use of stainless steel slags, specifically, as fillers in construction materials in particular asphalt or hydraulic mortar or concrete compositions, which are containing hydraulic or bituminous binding agents. The filler is produced by finely milling a coarser fraction of crushed steel slags which preferably has a relatively high content of steel (e.g. obtained by a magnetic separation process). The finely milled fractions obtained, having for example a particle size of less than 63 µm, have a smaller gamma dicalcium silicate content than the above described fines since it is produced starting from a coarser fraction of

the crushed steel slags so that they absorb much less water. However, these fillers are only used in small amounts in concrete and asphalt.

Therefore, there is a further need to provide environmentally friendly and economically practical methods in which large amounts of waste materials, in particular the fine fractions of crushed chromium containing steel slags, and/or milled chromium containing steel slags, can be used to produce economically valuable materials, in particular basement layers, and that in several fields of technology such as road engineering, building engineering, and construction and public works and whereby said materials have considerably reduced leaching of heavy metals and have compressive strengths of at least 2 MPa. .

SUMMARY OF THE INVENTION

The Applicant has now found surprisingly that it is possible to provide a method fulfilling the above mentioned needs.

It is thus an object of the present invention a method of producing a shape retaining mass having a compressive strength, measured in accordance with the ASTM standard test method D 698-12, of at least 2 MPa, comprising the steps of:

Step 1. mixing of a binder composition [composition (B), herein after] comprising at least one carbonating agent which is selected from a group consisting of potassium carbonate, potassium bicarbonate and a magnesium carbonate hydroxide hydrate compound of general formula (I): $xMgCO_3.yMg(OH)_2.zH_2O$ wherein x is a number in the range of 3.5 – 4.5, y is a number in the range of 0.5 – 1.5, and z is a number in the range of 3.5 – 5.5, with at least a particulate steel slag material, thereby forming a mixture [mixture M, herein after] and wherein said particulate steel slag material is containing calcium silicate phases and at least chromium and is present

in said mixture M in an amount of at least 50 % by dry weight (dry wt. %), relative to the total dry weight of the mixture M, and

Step 2. hardening of the mixture M, as obtained in Step 1., in the presence of water; thereby producing the shape retaining mass.

Another aspect of the present invention is directed to a shape retaining mass prepared according to the method of the invention.

Another aspect of the present invention is directed to the use at least one carbonating agent which is selected from a group consisting of potassium carbonate, potassium bicarbonate and a magnesium carbonate hydroxide hydrate compound of general formula (I): $xMgCO_3.yMg(OH)_2.zH_2O$ wherein x is a number in the range of 3.5 – 4.5, y is a number in the range of 0.5 – 1.5, and z is a number in the range of 3.5 – 5.5 for carbonation of a particulate steel slag material.

DETAILED DESCRIPTION OF EMBODIMENTS

The particulate steel slag material

In a preferred embodiment of the method according to the present invention the dry weight percent of the particulate steel slag material present in the mixture M of Step 1. is generally equal to or of at least 20 wt. %, preferably equal to or of at least 40 wt. %, more preferably equal to or of at least 60 wt. %, even more preferably equal to or of at least 75 wt. %, and most preferably equal to or of at least 80 wt. %, relative to the total dry weight of the mixture M of Step 1.

It is further understood that the dry weight percent of the particulate steel slag material present in the mixture M of Step 1. will generally be equal to or of at most 99 wt. %, more preferably equal to or of at most 95 wt. %, even more preferably equal to or of at most 90 wt. %,

most preferably equal to or of at most 88 wt. %, relative to the total dry weight of the mixture M of Step 1.

Good results were obtained when the mixture M of Step 1. comprised the particulate steel slag material in an amount of 70 dry wt. % - 95 dry wt. % relative to the total dry weight of the mixture M of Step 1.

In the rest of the text, when weight percentages are given in the present specification, these are percentages in dry weight.

As detailed above, in Step 1. of the method of the present invention use is made of particulate steel slag materials containing calcium silicate phases and at least chromium.

The particulate steel slag material containing calcium silicate phases and at least chromium suitable to be used in the method of the invention, may include notably the fine fractions of relatively slowly cooled steel and stainless steel slags, in particular special stainless steel slags produced during the production of chromium steel or nickel-chromium steel such as notably described in EP 2 160 367, EP 2 238 087 and WO 2009/090219, the whole content of those are herein incorporated by reference.

For the purpose of the present invention, the term “particulate steel slag material” is defined herein as any steel slag material which consists of loose particles. These particles may be of different sizes so that at least 50 vol.% of the particulate steel slag material has a particle size smaller than 1.0 mm, preferably smaller than 0.8 mm more preferably smaller than 0.5 mm. On the other hand, at least 50 vol.% of the particulate steel slag material has preferably a particle size larger than 1 µm, more preferably larger than 5 µm and most preferably larger than 10 µm.

A particular embodiment of the invention will now be described illustratively, but not restrictively, with reference to the following figures:

Fig. 1 is a diagram representing the phase transitions during the cooling of dicalcium silicate;

Fig. 2 is a flow chart representing a process for separating a fine stainless steel slag fraction from coarser fractions for use in the method of the present invention.

It is known that upon slow cooling of stainless steel slag particles which are comprising crystals of dicalcium silicate $(CaO)_2SiO_2$ in both their β and γ polymorphic states that when the crystalline dicalcium silicate cools down, it goes through several polymorphic forms as illustrated in Fig. 1:

α with hexagonal crystal structure,

α_H' with orthorhombic crystal structure,

α_L' with orthorhombic crystal structure,

β with monoclinic crystal structure, and

γ with orthorhombic crystal structure.

With pure dicalcium silicate under laboratory conditions, the transition from α_L'-dicalcium silicate to β-dicalcium silicate will occur at 675°C, then to be followed by the transition from β-dicalcium silicate to γ-dicalcium silicate at 490°C. As the transition from β-dicalcium silicate to γ-dicalcium silicate involves an increase of 12% in volume due to their different crystal structure, it causes high strains and microcracks in the dicalcium silicate crystals of the orthorhombic γ polymorphic state. These microcracks explain the disadvantageous water absorption properties that had been found hitherto in slag containing γ-dicalcium silicate, as water is absorbed by capillarity into them. The increase in volume in the transition from the β polymorphic state to the γ polymorphic state not only causes microcracks but even grain fracture and separation. As a result, the fine fraction of the slag will be disproportionately rich in comparatively soft γ-dicalcium silicate. Due to the abovementioned microcracks and the associated capillarity, this fine fraction of the slag will have a water

absorption capacity of over 20%. Moreover, it can retain this water for longer periods of time.

In the separation process, as illustrated in Fig. 2, molten slag is extracted from the stainless steel furnace 1 and brought to cooling pits 3. After cooling, the solidified slag will be dug from these cooling pits 3 and fed through a hopper 4. The hopper 4 comprises a grid for stopping all oversized slag pieces 6, in this particular case those bigger than 300 mm. As oversized pieces could damage the crushers used in the later process, these oversized pieces 6 are removed for later particular treatment, such as breaking with hammers and extraction of large metal fragments before being fed again through the hopper 4.

The slag particles smaller than 300 mm fall through the hopper 4 onto a first conveyor belt. This first conveyor belt then transports them through a first metal handpicking cabin 8 to a first crusher 9 and a first sieve 10. In the metal handpicking cabin 8, operators remove large metal pieces 11 from the slag particles on the conveyor belt. After the slag particles are crushed in the first crusher 9, they go through the first sieve 10 which separates them into three fractions: particles bigger than 35 mm, particles between 14 and 35 mm and particles smaller than 14 mm. The fraction of particles bigger than 35 mm is taken by a second conveyor belt through a second metal handpicking cabin 13 and a first metal separating magnetic belt 14, where more metal pieces 15 and 16 are removed. The particles bigger than 35 mm are then put back into the first crusher 9. The fraction of particles between 14 and 35 mm goes into a second crusher 17 and a second sieve 18, where after being crushed again it is separated into two fractions: a fraction of particles smaller than 14 mm and a fraction of particles bigger than 14 mm. The fraction of particles bigger than 14 mm is taken by a third conveyor belt through a second metal separating magnetic belt 20, where more metal 21 is removed, and back into the second crusher 17.

The fraction of particles smaller than 14 mm from the first sieve 10, and the fraction of particles smaller than 14 mm from the second sieve 18 join again and are put together through the third sieve 22, which separates them into a fraction 23 of particles smaller than 4 mm and a fraction of particles between 4 and 14 mm, this coarser fraction being suitable for use, for example, in construction materials.

Within the fraction 23 of particles smaller than 4 mm, a fine fraction 24 of particles smaller than 0.5 mm is particularly rich in γ-dicalcium silicate, as discussed above.

In one preferred embodiment of the method of the present invention, said fine fraction 24 of particles smaller than 0.5 mm are especially used in the method according to the invention.

If desired, the larger particles can also be further finely milled so as to obtain a milled material having a particle size distribution which shows a D_{10} value which is smaller than 100 µm, preferably smaller than 70 µm and more preferably smaller than 40 µm. Milling said coarser fractions of the slag material to a smaller particle size enables to recover more valuable steel from the slag material, in particular stainless steel. Preferably, the steel slag material which is milled is a steel slag fraction which still contains a relatively high amount of stainless steel.

Thus, the particulate steel slag material as used in Step 1. of the method according to the present invention may have a relatively high γ-dicalcium silicate content, in particular at least 3 wt. %, preferably at least 5 wt. % and more preferably at least 7 wt. % of γ-dicalcium silicate, and can thus be formed by the fines separated off from the crushed steel slag material.

The particulate steel slag material as used in Step 1. of the method according to the present invention has generally a relatively high basicity.

For the purpose of the present invention, the term "basicity" is intended to mean the ratio between the calcium content, expressed as wt.% CaO, as present in the particulate steel slag material and the silicon content, expressed as wt.% SiO_2, as present in the particulate steel slag material. The basicity is more particularly usually higher than 1.2, in particular higher than 1.4 and often higher than 1.6.

It is due to this high basicity that the dicalcium silicates, as detailed above, are formed upon a slow cooling of the steel slag, which is also responsible for the (partial) disintegration of the steel slag, i.e. to a so-called dusting or falling of the steel slag.

The particulate steel slag material as used in Step 1. of the method according to the present invention has generally a calcium content of at least 30%, in particular at least 40% by dry weight CaO and a silicon content of at least 15%, in particular at least 20% by dry weight SiO_2 (the calcium and silicon contents are based on the molecular weight of CaO and SiO_2 respectively but it is generally understood that the calcium and silicon do not have to be present in their oxide form but are in particular in other amorphous or crystalline phases, in particular in silicates.

The particulate steel slag material as used in Step 1. of the method according to the present invention comprises preferably more than 50% by dry weight, more preferably more than 60% by dry weight and most preferably more than 70% by dry weight of crystalline phases, the remaining phases being amorphous.

The particulate steel slag material as used in Step 1. of the method according to the present invention has generally a pH of at least 8.5, in particular at least 10, and even more particular at least 11.

The pH has been measured after immersion of the shape retaining mass in demineralised water during 24 hours in a liquid/volume ratio of 10.

The particulate steel slag material of the method according to the present invention usually contains substantial amounts of heavy metals such as chromium, in particular chromium VI in the form of CrO_4^{-2} and $Cr_2O_7^{-2}$ and often also molybdenum in anionic form such as MnO_4^{-2}, which constitute a significant environmental and public health problem.

Molybdenum (Mo) and chromium (Cr) present in the particulate steel slag material can be very mobile and can hence be subjected to prompt leaching from the slag. By consequence, the slag cannot be disposed of in ordinary landfills; it should be treated as special waste, which makes disposal more costly.

The Inventors have surprisingly found that the method according to the invention is especially effective in the immobilization of Cr and Mo, as present in the particulate steel slag material, in the final shape retaining mass, in particular road construction materials.

Advantageously, said particulate steel slag material may comprise in particular at least 1000 ppm, more particularly at least 3000 ppm and even more particularly at least 5000 ppm of chromium.

Advantageously, said particulate steel slag material may comprise in particular at least 100 ppm, in particular at least 1000 ppm, and more particularly at least 2500 ppm of molybdenum.

The particulate steel slag material of the present invention may also comprise nickel (Ni). Typically, said particulate steel slag material can comprise at least 300 ppm nickel, in particular at least 400 ppm nickel and more particularly at least 500 ppm nickel.

The composition (B)

In a preferred embodiment of the method according to the present invention the dry weight percent of the composition (B) present in the mixture M of Step 1. is generally of at least 1 wt. %, preferably at least 5 wt. %, preferably at least 8 wt. %, more preferably at least 10 wt. %, and

even more preferably at least 12 wt. %, relative to the total dry weight of the mixture M of Step 1.

It is further understood that the dry weight percent of the composition (B) present in the mixture M of Step 1. is generally at most 45 wt. %, more preferably at most 35 wt. %, more preferably at most 30 wt. %, even more preferably at most 25 wt. %relative to the total dry weight of the mixture M of Step 1.

Good results were obtained when the mixture M of Step 1. comprised the composition (B) in an amount of 5 dry wt. % - 30 dry wt. % the total dry weight of the mixture M of Step 1.

In the rest of the text, the expression "carbonating agent" is understood, for the purposes of the invention, both in the plural and the singular, that is to say that the composition (B) may comprise one or more than one carbonating agent.

In one embodiment of the method according to the present invention, the composition (B) mixed with the particulate steel slag material in Step 1. consists essentially of the carbonating agent, as detailed above.

For the purpose of the present invention, the expression "consists essentially of" is intended to denote that any additional ingredient different from the carbonating agent, as detailed above, is present in an amount of at most 1 % by weight, based on the total weight of the carbonating agent in the composition (B).

In another embodiment of the present invention, the composition (B) mixed with the particulate steel slag material in Step 1. of the method of the present invention comprises a carbonating agent in an amount advantageously of above 1 wt. % more preferably above 5 wt. %, more preferably above 10 wt. %, more preferably above 15 wt. %; more preferably above 20 wt. %, more preferably above 25 wt. %, , based on the total weight of the composition (B). It is further understood that the

weight percent of the carbonating agent in the composition (B) will generally be at most 99 wt. %, preferably at most 95 wt. %, preferably at most 90 wt. %, more preferably at most 80 wt. %, more preferably at most 75 wt. %, , based on the total weight of the composition (B).

Good results were obtained when the mixture M of Step 1. comprised the carbonating agent in an amount of at least 1 dry wt. %, preferably at least 2 dry wt. %, more preferably at least 3 dry wt. %, relative to the total dry weight of the mixture M of Step 1.

According to certain preferred embodiments of the method according to the present invention the carbonating agent comprises a magnesium carbonate hydroxide hydrate compound of general formula (I): $xMgCO_3.yMg(OH)_2.zH_2O$ wherein x is a number in the range of 3.5 – 4.5, preferably x is 4, y is a number in the range of 0.5 – 1.5, preferably y is 1 and z is a number in the range of 3.5 – 5.5, preferably z is 4 or 5.

Preferred magnesium carbonate hydroxide hydrate compounds are chosen among hydromagnesite (i.e. $4MgCO_3.Mg(OH)_2.4H_2O$) and dypingite (i.e. $4MgCO_3.Mg(OH)_2.5H_2O$).

The magnesium carbonate hydroxide hydrate compounds of general formula (I) are known in the art. They can be manufactured according to known methods in the art. Generally they can be made by exposure of magnesium compounds, e.g. MgO or $Mg(OH)_2$ (or mixtures thereof) to CO_2 under a variety of conditions.

For example, EP 2 508 496 describes the use of these hydrated magnesium carbonate compounds of formula (I) in binders which are based on the formation of magnesium silicate hydrates (MSH) and used to formulate a concrete, mortar or plaster and other construction chemical products. These binders can be used to replace the known binders Portland cement, high alumina cement and the like. According to the teachings of EP 2 508 496, the amount of extra calcium compounds, e.g. $Ca(OH)_2$ and/or CaO, has to be limited, because these calcium ions

are forming calcite in the presence of hydromagnesite (i.e. $4MgCO_3.Mg(OH)_2.4H_2O$), which results in a decrease of its efficacy.

The Inventors have now surprisingly found that despite the high content of CaO in the particulate steel slag material, as detailed above, the hydrated magnesium carbonate compounds of formula (I) can act as very efficient carbonating agents and reduce leaching of heavy metals, in particular chromium and molybdenum in the final shape retaining mass.

WO 2009/156740 also describes the use of these hydrated magnesium carbonate compounds of formula (I) in admixture with magnesia as a binder composition used to make construction products.

The Inventors has now found that compared to Portland cement these binder compositions provide an improved leaching behaviour of heavy metals, in particular of chromium and molybdenum, notwithstanding the fact that they have a considerably lower pH than Portland cement.

Comparative tests have indeed been carried out wherein varying amounts of different cements (CEM I, CEM II and CEM IIIb) have been mixed with stainless steel slag fines (0 – 0.5 mm). At the natural pH of the mixtures, i.e. at a pH of about 12.8, large amounts of cement were needed (cement to aggregate ratios of 0.5 or even higher) to keep the leaching of chromium below the limit of 0.10 mg/l and the leaching of molybdenum below the limit of 0.15 mg/l. The tests also revealed that when acidifying the water used to do the leaching tests so that the final pH approaches pH 12, the leaching of both chromium and molybdenum considerably increased. With the method of the present invention, on the contrary, low leaching values are achieved for lower final pH values.

According to another preferred embodiment of the method according to the present invention the carbonating agent comprises potassium carbonate and/or potassium bicarbonate.

According to a preferred embodiment of the method according to the present invention, the carbonating agent in Step 1. can further comprise a carbonation enhancing compound selected from the group consisting of magnesium oxide (MgO), calcium oxide (CaO), calcium magnesium oxide (i.e calcined dolomite), and mixtures thereof , preferably MgO.

The molar ratio of said carbonation enhancing compound to the carbonating agent is advantageously of at least 1,0, preferably at least 1.5, more preferably at least 3.0. It is further understood that the molar ratio of said carbonation enhancing compound to the carbonating agent will generally be at most 10, preferably at most 8 and more preferably at most 6.

In an advantageous embodiment of the present invention, the composition (B) mixed with the particulate steel slag material in Step 1. of the method of the present invention further comprises a gel forming binder composition in an amount advantageously above 1 wt. %, preferably above 10 wt. %, more preferably above 20 wt. %, more preferably above 30 wt. %, based on the total weight of the composition (B). It is further understood that the weight percent of said gel forming binder composition in the composition (B) will generally be of at most 99 wt. %, preferably of at most 95 wt. %, more preferably at most 80 wt. %, more preferably at most 70 wt. %, based on the total weight of the composition (B).

The gel forming binder composition comprises a glass compound and said glass compound is containing more than 50 % by dry weight of SiO_2.

Alternatively, the gel forming binder composition consists of the glass compound.

Non limitative examples of suitable glass compounds may include, but not limited to, industrial silicated glass, such as hollow glasses

(from bottles, cups, etc.) or flat glass, different from natural silicate glasses (such as pozzolana, tuff , pumice) or any other industrial silicate glasses (especially such as blast furnace slag, silica fume, fly ash from thermal power plants), as notably described in EP 1250397 B1, its whole content is herein incorporated by reference,

In an advantageous embodiment of the method according to the present invention, the glass compound comprises however glass powder, in particular soda-lime glass powder. The glass powder comprises preferably comminuted glass cullet particles.

Glass cullet is a waste product comprising industrial silicate glass and flat and hollow (container) glass that cannot be introduced in a furnace to be valorised. The glass powder used in the method according to the present invention comprises preferably more than 60% more preferably more than 65% by dry weight of SiO_2.

In another advantageous embodiment of the method according to the present invention, the glass compound is silica fume. Silica fume is an amorphous polymorph of silicon dioxide. It is an ultrafine powder containing more than 85% by dry weight of SiO_2. As it contains no or nearly no CaO, only silica-gel is formed in the absence of CaO.

In another advantageous embodiment of the method according to the present invention, the glass compound is fly ash, such as Class C and Class F fly ash.

It is known that under alkaline conditions, such glass compounds are activated thereby producing a silica-gel material which provides a high mechanical strength to a finished product. Due to the alkaline nature of the particulate steel slag material of the present invention, as detailed above, the production of said silica-gel material may also occur upon mixing with said particulate steel slag material thereby forming a finished product having a high mechanical strength. However,

such a finished product suffers dramatically from leaching of heavy metals, in particular chromium and molybdenum.

The Inventors have now found that the combined use of the binding ability of a cheaper gel forming binder composition with the carbonating agent, in particular a magnesium carbonate hydroxide hydrate compound of general formula (I) provides a less costly method for producing a final shape retaining mass still having a suitable mechanical strength and having a strongly reduced leaching of the heavy metals, in particular chromium and molybdenum.

If desired, the gel forming binder composition, as detailed above, is completed by adding to the glass compound at least one basic reagent suitable to activate the glass compound before being mixed with the particulate steel slag material in Step 1. of the method of the present invention and/or after being mixed with the particulate steel slag material in Step 1. of the method of the present invention. This is especially advantageous when particulate steel slag material has a reduced pH, for example by having been weathered for some time, i.e. by natural carbonation.

Advantageously, the dry weight ratio of the glass compound to the basic reagent is greater than 3, preferably greater than 4, more preferably greater than 5.

Non limitative examples of suitable basic reagent may include, but not limited to, sodium and/or potassium hydroxide and/or calcium hydroxide, lime, cement, in particular blast furnace cement.

In another preferred embodiment of the method according to the present invention, the composition (B) mixed with the particulate steel slag material in Step 1. consists essentially of the carbonating agent, as detailed above, and the gel forming binder composition, as detailed above.

For the purpose of the present invention, the expression "consists essentially of" are intended to denote that any additional ingredient different from the carbonating agent, as detailed above, and the glass binder, as detailed above. is present in an amount of at most 1 % by weight, based on the total weight of the carbonating agent in the composition (B).

The Inventors have thus found that the presence of the gel forming binder composition enables to reach suitable mechanical strength and the carbonating agent enables to control the leachability, over time, of the heavy metals contained in the shape retaining mass. Moreover, the combination of the gel forming binder composition with the carbonating agent allows to reduce the amount of the carbonating agent in the mixture without affecting the final properties of the shape retaining mass in terms of compressive strength and leachability.

Reducing agent

According to certain embodiments in Step 1. of the method according to the present invention, a reducing agent, in particular a chromium reducing agent capable of transforming hexavalent chromium into a trivalent chromic form by donating one or more electrons, may be added.

The Applicant has found that the addition of reducing agents in Step 1. of the method of the invention further improves the retention of chromium in the final shape retaining mass, i.e. the finished product.

Said reducing agent may be added to the composition (B), as detailed above, prior to mixing with the particulate steel slag materials or may be added to the particulate steel slag materials, as detailed above, prior to mixing with the composition (B) or may be added to the mixture M formed in Step 1. prior to hardening of said mixture M. Non limitative examples of suitable reducing agents may notably include ferrous sulphate

($FeSO_4$), in particular ferrous sulfate heptahydrate ($FeSO_4.7H_2O$), stannous chloride ($SnCl_2$), stannous sulphate ($SnSO_4$), stannous oxide (SnO), stannous hydroxide ($Sn(OH)_2$), stannous manganese sulphate , iron sulphide (FeS), and/or ferrous chloride ($FeCl_2$), in particular ferrous chloride tetrahydrate ($FeCl_2.4H_2O$) and combinations thereof. Preferred reducing agents are $FeSO_4.7H_2O$, $SnSO_4$, $SnCl_2$, SnO, $Sn(OH)_2$ and combinations thereof.

The dry weight percent of the reducing agent in the mixture M is generally at least 0.01 wt. %, preferably at least 0.03 wt. %, more preferably at least 0.25 wt. %, even more preferably at least 0.50 wt. %, most preferably at least 1.00 wt. %, based on the total dry weight of the particulate steel slag material.

It is further understood that the dry weight percent of the reducing agent in the mixture M will generally be at most 8.0 wt. %, more preferably at most 6.0 wt. %, most preferably at most 5.0 wt. %, based on the total dry weight of the particulate steel slag material.

Good results were obtained when the mixture M comprised the reducing agent in an amount of 0.03 wt. % - 5.00 wt. % based on the total dry weight of the particulate steel slag material.

Other ingredients

According to certain embodiments in Step 1. of the method according to the present invention, other ingredients, may be added to improve further the final properties of the shape retaining mass according to its desired end use.

Said other ingredients may be added to the composition (B), as detailed above, prior to mixing with the particulate steel slag material or may be added to the particulate steel slag material, as detailed above, prior to mixing with the composition (B) or may be added to the mixture M formed in Step 1. prior to hardening of said mixture M in Step 2.. Suitable

other ingredients may notably include, but not limited to (i) fine and/or coarse aggregates having a particle size larger than the particle size of the particulate steel slag material such as notably sand, natural gravel, crushed stone and the like; (ii) inert filler.

The dry weight percent of the other ingredients in the mixture M is generally equal to or at least 0.01 wt. %, preferably equal to or at least 0.03 wt. %, more preferably equal to or at least 0.25 wt. %, even more preferably equal to or at least 0.50 wt. %, most preferably equal to or at least 1.00 wt. %, based on the total dry weight of the mixture M.

It is further understood that the dry weight percent of the other ingredients in the mixture M will generally be equal to or at most 79 wt. %, preferably equal to or at most 50 wt. %, more preferably equal to or at most 30.0 wt. %, most preferably equal to or at most 10 wt. %, based on the total dry weight of the mixture M.

In Step 1. of the method according to the present invention, the particulate steel slag material, as detailed above, the carbonating agent, as detailed above, optionally the gel forming binder composition, as detailed above, optionally the reducing agent, as detailed above, and optionally the other ingredients are mixed as to obtain an homogeneous mixture M according to known practice in the art.

Prior to Step 2., it is preferred to compact the mixture (M) by means of a compactor, in particular by means of a roller-compactor (i.e. a so-called road roller). The mixture (M) is first spread in a layer and this layer is then compacted before it has hardened.

In Step 2. of the method of the present invention, the hardening of the mixture M, as obtained in Step 1., occurs in the presence of water and the amount of water relative to total dry weight of the mixture M is advantageously equal to or at least 5 wt. %, preferably equal to or at least 10 wt. %, more preferably equal to or at least 15 wt. %.

When the particulate steel slag material as used in the method according the invention, is too dry then additional water may be added to the particulate steel slag materials, as detailed above, or may be added to the composition (B), as detailed above, prior to mixing with the particulate steel slag materials or may be added to the mixture M.

Alternatively, when the particulate steel slag material as used in the method according the invention, is having a too high water content then the particulate steel slag material can be dried according to methods known in the art.

The shape retaining mass

As said, another aspect of the present invention is directed to a shape retaining mass prepared according to the method of the invention, as described in detail above.

The shape retaining mass according to the invention advantageously has a compressive strength higher than 2 MPa, with a compressive strength of higher than 3 MPa being preferred and a compressive strength of higher than 4 MPa being particularly preferred wherein a compressive strength is measured in accordance with the ASTM standard test method D 698-12. More advantageously, it has a compressive strength falling in the range between 2 MPa and 50 MPa.

The shape retaining mass according to the invention advantageously has a Cr and/or Ni leaching of less than 0.5 mg/L, preferably less than 0.30 mg/L, more preferably less than 0.20 mg/L, even more preferably less than 0.10 mg/L, the leaching test of the shape retaining mass being measured according to DIN 38414-S4/EN 12457-4.

The shape retaining mass according to the invention advantageously has a Mo leaching of less than 1.0 mg/L, preferably less than 0.50 mg/L, more preferably less than 0.20 mg/L, even more preferably

less than 0.10 mg/L, the leaching test of the shape retaining mass being measured according to DIN 38414-S4/EN 12457-4.

A preferred use of a shape retaining mass of the invention is as a construction material, in particular a road construction material such as basement or subbasement depending on the compressive strength obtained.

The Inventors have surprisingly found that the shape retaining mass of the invention comprises calcite ($CaCO_3$).

Without being bound to this theory, the formation of calcite might be the result of the reaction of the amorphous phases of particulate steel slag material with the carbonating agent of the present invention. Moreover, besides this production of calcite, it has also been surprisingly observed that multiple crystalline phases are also produced, including in particular the neo-formed phases magnesiochromite and magnesium chromium carbonate hydrates. The presence of these crystalline phases might enable to fix some heavy metals, particularly chromium, more preferably chromium and/or nickel, in the structure thereof. In that way, the leachability of the shape retaining mass can be sufficiently controlled over time since heavy metals are fixed in the crystalline structures.

EXPERIMENTAL TEST RESULTS

The invention will be now described in more details with reference to the following examples, whose purpose is merely illustrative and not intended to limit the scope of the invention.

General procedure for producing a shape retaining

A shape retaining mass was produced by mixing the particulate steel slag material (i.e. stainless steel slag fines (0 - 0.5 mm)) with a carbonating agent, optionally a reducing agent, optionally a gel forming binder composition, optionally other ingredients and water. The amounts of the different ingredients are summarized in Tables 1 to 3. Specimens were made from this mixture by compacting it in a mould having

an internal diameter of 54.8 mm and a height of 50 mm. with a pressure of 10 MPa.

The addition of water enables to achieve the required water/solid ratio and to obtain a homogeneous mixture.

The Proctor values of the different mixtures were determined, i.e. the water content at which in a Proctor test the highest dry density is obtained. Moisture contents which were close to this Proctor value were used in all the experimental test, as summarized in Tables 1 – 3.

The compressive strength of the pastilles of all comparative examples C1, C2, C23 and C24 and examples 2 -22, 25 and 26 was measured after 21 days with a Controlab hydraulic press of type E0160S and in accordance with the ASTM standard test method D 698-12.

All the leachate analysis tests of the shape retaining mass of all comparative examples C1, C2, C23 and C24 and examples 2 -22, 25 and 26 were measured according to standard DIN 38418-S4.

All experimental results are summarized in Tables 1, 2 and 3.

Table 1:

EXAMPLE NUMBER	C1	C2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Mixture M	**% of total dry weight of the total mixture M**															
Slag (0 - 0.5 mm)	100	85	88.3	88.3	88.3	85	85	85	85	85	85	85	85	85	85	85
Composition (B)	0	15	11.7	11.7	11.7	15	15	15	15	15	15	15	15	15	15	15
Reducing agent	**% of slag (0/0.5 mm)**															
$FeSO_4.7H_2O$	0	0	0	0	0	0	0.1	1	5	0	1	0.25	0.03	0.03	0.03	0.5
Composition (B)	**molar ratio**															
(MgO) or (CaO) / $4MgCO_3.Mg(OH)_2.5H_2O$	0	0	0	3.43	3.43	3.43	3.43	3.43	3.43	3.43	3.43	3.43	3.43	3.43	3.43	3.43
	% of the total weight of composition (B)															
$MgO+4MgCO_3.Mg(OH)_2.5H_2O$	0	0	14.5	14.5	0	100	100	100	100	33.3	33.3	33.3	33.3	33.3	33.3	33.3
$CaO+4MgCO_3.Mg(OH)_2.5H_2O$	0	0	0	0	14.5	0	0	0	0	0	0	0	0	0	0	0
Gel forming binding composition	0	100	85.5	85.5	85.5	0	0	0	0	66.7	66.7	66.7	66.7	66.7	66.7	66.7
Gel forming binding composition	**% of the total weight of the glass binder**															
Glass cullet	0	85	95	95	95	0	0	0	0	95	95	95	95	95	95	95
NaOH	0	15	0	0	0	0	0	0	0	0	0	0	0	0	0	0
$Ca(OH)_2$	0	0	5	5	5	0	0	0	0	5	5	5	5	0	0	0
Cement CEM I	0	0	0	0	0	0	0	0	0	0	0	0	0	5	0	0
Cement CEM III A	0	0	0	0	0	0	0	0	0	0	0	0	0	0	5	5
Moisture	**%**															
True Water/Solid ratio	12.1	16.2	20.6	20.8	21.9	18.1	17.8	18.7	19.9	18.0	?	18.0	18.0	18.0	18.0	18.0
Compressive strength of the mass	**MPa**															
σ_c (21 days)	2.0	9.8	4.7	4.5	4.1	7.6	7.4	7.3	8.3	7.2	2.3	3.2	5.2	4.9	4.9	5.7
Leachate Content (mg/L)																
Cr	0.67	2.80	0.17	0.18	0.16	0.2	0.1	0.1	< 0.1	0.34	< 0.1	0.23	0.26	0.30	< 0.1	< 0.1
Mo	0.51	1.40	0.25	0.27	0.25	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Ni	0.3	-	< 0.1	< 0.1	< 0.1	0.3	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
pH mixture M	-	-	11.5	11.7	11.6	11.3	11.6	11.2	11.1	11.1	11.4	10.9	10.9	11.0	10.9	10.7
pH final mass	-	12.8	12.5	12.5	12.7	11.8	11.6	11.9	11.7	12.1	12.1	12.0	12.5	12.6	12.1	11.9

Table 2:

Example Number	17	18	19	20	21	22
Mixture M	% of total dry weight of the total mixture M					
Slag (0 - 0.5 mm)	85	85	85	86	86	87.5
Composition (B)	15	15	15	14	14	12.5
Reducing agent	% of slag (0/0.5 mm)					
$FeSO_4.7H_2O$	0	0	0	0.25	0	0
$SnSO_4$	0.5	0	0	0	0	0.05
$SnCl_2$	0	0	0	0	0.05	0
$Sn(OH)_2$	0	0.25	0	0	0	0
SnO	0	0	0.25	0	0	0
Composition (B)	molar ratio					
(MgO) / $4MgCO_3.Mg(OH)_2.5H_2O$	3.43	3.43	3.43	3.43	3.43	3.43
	% of the total weight of composition (B)					
$MgO+4MgCO_3.Mg(OH)_2.5H_2O$	33.3	33.3	33.3	28.6	28.6	20.0
Gel forming binding composition	66.7	66.7	66.7	71.4	71.4	80.0
Gel forming binding composition	% of the total weight of the glass binder					
Glass cullet	95	95	95	95	95	95
NaOH	0	0	0	0	0	0
$Ca(OH)_2$	5	5	5	0	5	0
Cement CEM I	0	0	0	0	0	0
Cement CEM III A	0	0	0	5	0	5
Moisture	%					
True Water/Solid ratio	18.0	18.0	18.0	17.0	17.0	17.0
Compressive strength of the mass	MPa					
σc (21 days)	5.9	3.6	3.0	4.0	3.7	3.3
Leachate Content (mg/L)						
Cr	< 0.1	< 0.1	< 0.1	0.17	0.17	< 0.1
Mo	< 0.1	< 0.1	< 0.1	0.13	0.21	0.24
Ni	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
pH mixture M	10.7	10.8	10.8	11.2	11.3	11.7
pH final mass	12.0	12.0	12.1	12.3	12.0	12.3

Table 3:

Example Number	C23	C24	25	26
Mixture M	% of total dry weight of the total mixture M			
Slag (0/0.5 mm)	85	85	85	85
Composition (B)	15	15	15	15
Reducing agent	% of slag (0/0.5 mm)			
$FeSO_4.7H_2O$	0	5	5	1
Composition (B)	% of the total weight of composition (B)			
MgO + K_2CO_3[a]	0	0	100	0
MgO + $NaHCO_3$[a]	33.3	100	0	0
MgO + $4MgCO_3.Mg(OH)_2.5H_2O$[a]		0	0	100
Limestone filler	0	0	0	4.5
Gel forming binding composition	66.7	0	0	0
Gel forming binding composition	% of the total weight of the glass binder			
Glass cullet	85	0	0	0
NaOH	15	0	0	0
$Ca(OH)_2$	0	0	0	0
Cement CEM I	0	0	0	0
Cement CEM III A	0	0	0	0
Moisture	%			
True Water/Solid ratio	16.2	18.0	16.1	18.0
Compressive strength of the mass	MPa			
σc (21 days)	8.3	1.1	5.3	6.0
Leachate Content (mg/L)				
Cr	2.7	0.1	0.1	< 0.1
Mo	1.4	0.7	1.0	< 0.1
Ni	-	< 0.1	< 0.1	< 0.1
pH mixture M	-	12.1	11;7	10.8
pH final mass	12.9	12.3	12,4	12.2

[a]molar ratio of MgO to K_2CO_3, $NAHCO_3$ or $4MgCO_3.Mg(OH)_2.5H_2O$ is 3.43

Experiment 27

Mineralogical analysis was carried out by XRD (x-ray diffraction) for the shape retaining mass of example 9 and for the particulate stainless steel slag (i.e. Slag (0/0.5 mm)) used for the manufacturing of said shape retaining mass. The results are summarized in Table 4.

Table 4: semi-quantitative mineralogical analysis of Slag (0/0.5 mm) before mixing and of the shape retaining mass of example 9.

Compounds	**Chemical formula**	**Slag (0/0.5 mm) (%)**	**Ex. 9 (%)**
Amorphous	/	25	10
Akermanite-Gehlenite	$Ca_2(Al_{.25}Mg_{.75})((Al_{.25}Si_{.75})O_7)$	5	/
Bredigite	$Ca_{14}Mg_2(SiO_4)_8$	14	14
Brownmillerite	$Ca_2(Al, Fe^{+3})_2O_5$	<5	/
Brucite	$Mg(OH)_2$	/	<5
Calcio-olivine	$CaSiO_4$	10	11
Calcite	$CaCO_3$	<5	17
Calcium aluminium sulphate hydrate	$Ca_4Al_2O_6SO_4.14H_2O$	/	<5
Cuspidine	$Ca_4Si_2O_7F_2$	11	/
Enstatite	$MgSiO_3$	/	6
Enstatite, Ferroan	$Fe_{.155}Mg_{.845}SiO_3$	/	/
Ferrinatrite	$Na_3Fe(SO_4)_3.12(H_2O)$	/	/
Gypsum	$Ca(SO_4).2(H_2O)$	<5	<5
Magnesiochromite	$Fe_{.13}Mg_{.87}Cr_2O_4$	/	<5
Magnesiochromite, ferroan	$(Mg_{.8}Fe_{.2})Cr_2O_4$	<5	/
Magnesium chromium carbonate hydrate	$MgCr(CO_3)_2.3(H_2O)$	/	<5
Manganilvaite	$(Ca_{.98}Mn_{.02})Fe_2(Mn_{.72}Fe_{.28}(Si_2O_7)O(OH)$	/	<5
Mayenite	$Ca_{12}Al_{14}O_{33}$	<5	/
Melilite	$Ca_2Mg_{.75}Al_{.5}Si_{1.75}O_7$	/	5
Merwinite	$Ca_3Mg(SiO_4)_2$	17	13
Periclase	MgO	<5	<5
Quartz	SiO_2	<5	<5
Rutile	TiO_2	<5	/
Sodium aluminate silicate	$Na_{1.04}Al_2Si_{48}O_{99.52}$	/	/
Wollastonite	$CaSiO_3$	<5	/

As it can be seen from Table 4, the Inventor has now found that the chromium is located in stable structures as magnesiochromite, magnesium chromium carbonate hydrate upon carbonation with the carbonating agent of the present invention thereby preventing effectively the leaching of chromium. Moreover, the content of calcite increases from an amount of less than 5 % to an amount of 17 %, whilst the amount of amorphous phases decreases from 25 to 10%, thereby providing good mechanical properties.

CLAIMS

1. A method of producing a shape retaining mass having a compressive strength, measured in accordance with the ASTM standard test method D 698-12, of at least 2 MPa, comprising the steps of:

Step 1. mixing of a binder composition [composition (B), herein after] comprising at least one carbonating agent which is selected from the group consisting of potassium carbonate, potassium bicarbonate and magnesium carbonate hydroxide hydrate compounds of general formula (I): $xMgCO_3.yMg(OH)_2.zH_2O$ wherein x is a number in the range of 3.5 – 4.5, y is a number in the range of 0.5 – 1.5, and z is a number in the range of 3.5 – 5.5, with at least a particulate steel slag material, thereby forming a mixture [mixture M, herein after] and wherein said particulate steel slag material is containing calcium silicate phases and at least chromium and is present in said mixture M in an amount of at least 50 % by dry weight (dry wt. %), relative to the total dry weight of the mixture M, and

Step 2. hardening of the mixture M, as obtained in Step 1., in the presence of water, thereby producing the shape retaining mass.

2. The method according to claim 1, characterized in that the particulate steel slag material is present in an amount of 70 - 95 dry wt. % based on the total dry weight of the mixture M.

3. The method according to claim 1 or claim 2, characterized in that at least 50 vol.% of the particulate steel slag material has a particle size smaller than 1.0 mm.

4. The method according to any one of the claims 1 to 3, characterized in that the particulate steel slag material is comprising γ-

dicalcium silicate in an amount of at least 3 wt. % relative to the total dry weight of the particulate steel slag material.

5. The method according to any one of the claims 1 to 4, characterized in that the particulate steel slag material has a calcium content, expressed as % CaO, of at least 30% by dry weight and a silicon content, expressed as % SiO_2, of at least 15% by dry weight.

6. The method according to any one of the claims 1 to 5, characterized in that the particulate steel slag material has a pH of at least 8.5.

7. The method according to any one of the claims 1 to 6, characterized in that the particulate steel slag material has a chromium content of at least 1000 ppm, more particularly of at least 3000 ppm, even more particularly of at least 5000 ppm.

8. The method according to any one of the claims 1 to 7, characterized in that the particulate steel slag material has a molybdenum content of at least 100 ppm, in particular at least 1000 ppm, and more particularly at least 2500 ppm.

9. The method according to any one of the claims 1 to 8, characterized in that the particulate steel slag material has a nickel content of at least 300 ppm, in particular at least 400 ppm, and more particularly at least 500 ppm.

10. The method according to any one of the claims 1 to 9, characterized in that the composition (B) is present in mixture M in an amount of at least 1 wt. %, preferably at least 5 wt. %, more preferably at least 10 wt. % and the composition (B) being preferably present in mixture M in an amount of at most 45 wt. %, more preferably at most 35 wt. %, based on the total dry weight of the mixture M.

11. The method according to any one of the claims 1 to 10, characterized in that the composition (B) consists essentially of the carbonating agent or comprises the carbonating agent in an amount

above 1 wt. % preferably above 5 wt. %, more preferably above 10 wt. % based on the total weight of the composition (B).

12. The method according to any one of the claims 1 to 11, characterized in that the carbonating agent comprises at least one magnesium carbonate hydroxide hydrate compound of general formula (I): $xMgCO_3.yMg(OH)_2.zH_2O$ wherein x is 4, y is 1 and z is 4 or 5.

13. The method according to any one of the claims 1 to 12, characterized in that the carbonating agent comprises potassium carbonate and/or potassium bicarbonate.

14. The method according to any one of the claims 12 to 13, characterized in that the carbonating agent further comprise a carbonation enhancing compound selected from the group consisting of magnesium oxide (MgO), calcium oxide (CaO), calcium magnesium oxide (i.e calcined dolomite), and mixtures thereof, preferably MgO.

15. The method according to claim 14, characterized in that the molar ratio of The molar ratio of said carbonation enhancing compound to the carbonating agent is advantageously of at least 1,0, preferably at least 1.5, more preferably at least 3.0.

16. The method according to any one of the claims 1 to 15, characterized in that the composition (B) further comprises a gel forming binder composition in an amount of above 1 wt. %, preferably above 10 wt. %, more preferably above 20 wt. % and the composition (B) preferably comprising said gel forming binder composition in an amount of at most 99 wt. %, preferably at most 95 wt. %, more preferably at most 80 wt. %, based on the total weight of the composition (B).

17. The method according to claim 16, characterized in that the gel forming binder composition comprises a glass compound which contains more than 50 % by dry weight of SiO_2.

18. The method according to claim 17, characterized in that glass compound comprises glass powder, in particular a soda-lime glass powder.

19. The method according to any one of the claims 1 to 18, characterized in that a reducing agent capable of transforming hexavalent chromium into a trivalent chromic form by donating one or more electrons is added in Step 1. and wherein said reducing agent is preferably selected from the group consisting of ferrous sulphate ($FeSO_4$), in particular ferrous sulfate heptahydrate ($FeSO_4.7H_2O$), stannous chloride ($SnCl_2$), stannous sulphate ($SnSO_4$), stannous oxide (SnO), stannous hydroxide ($Sn(OH)_2$), stannous manganese sulphate , iron sulphide (FeS), and/or ferrous chloride ($FeCl_2$), in particular ferrous chloride tetrahydrate ($FeCl_2.4H_2O$) and combinations thereof.

20. The method according to any one of the claims 1 to 19, characterized in that prior to Step 2., the mixture (M) is compacted by means of a compactor, in particular by means of a roller-compactor.

21. A shape retaining mass prepared according to the method according to any one of the claims 1 to 20.

22. A shape retaining mass according to claim 21, wherein said shape retaining mass has a compressive strength higher than 2 MPa, preferably higher than 3 MPa, more preferably higher than 4 MPa, the compressive strength value being measured in accordance with the ASTM standard test method D 698-12.

23. A shape retaining mass according to claim 21 or 22, wherein the Cr and/or Ni leaching from the shape retaining mass is less than 0.5 mg/L, preferably less than 0.30 mg/L, more preferably less than 0.20 mg/L, even more preferably less than 0.10 mg/L, the leaching test of the shape retaining mass being measured according to DIN 38414-S4/EN 12457-4.

24. A shape retaining mass according to any one of the claims 21 to 23, wherein the Mo leaching from the shape retaining mass is less than 1.0 mg/L, preferably less than 0.50 mg/L, more preferably less than 0.20 mg/L, even more preferably less than 0.10 mg/L, the leaching test of the shape retaining mass being measured according to DIN 38414-S4/EN 12457-4.

25. A basement or sub-basement layer comprising the shape retaining mass according to any one of the claims 21 to 24.

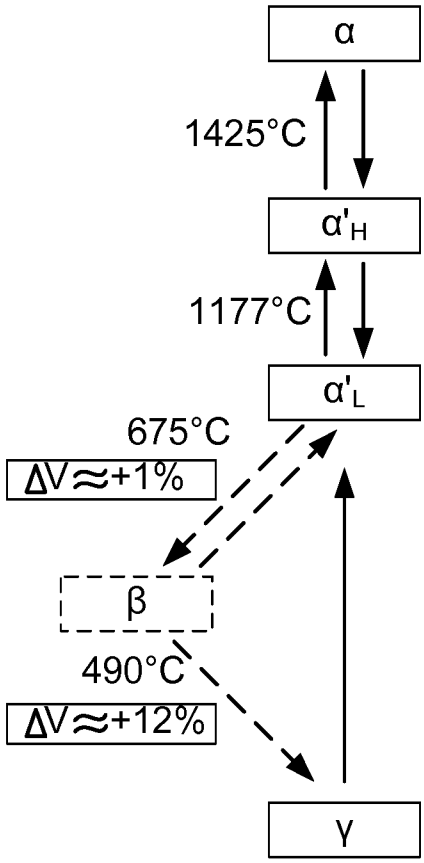


Fig. 1

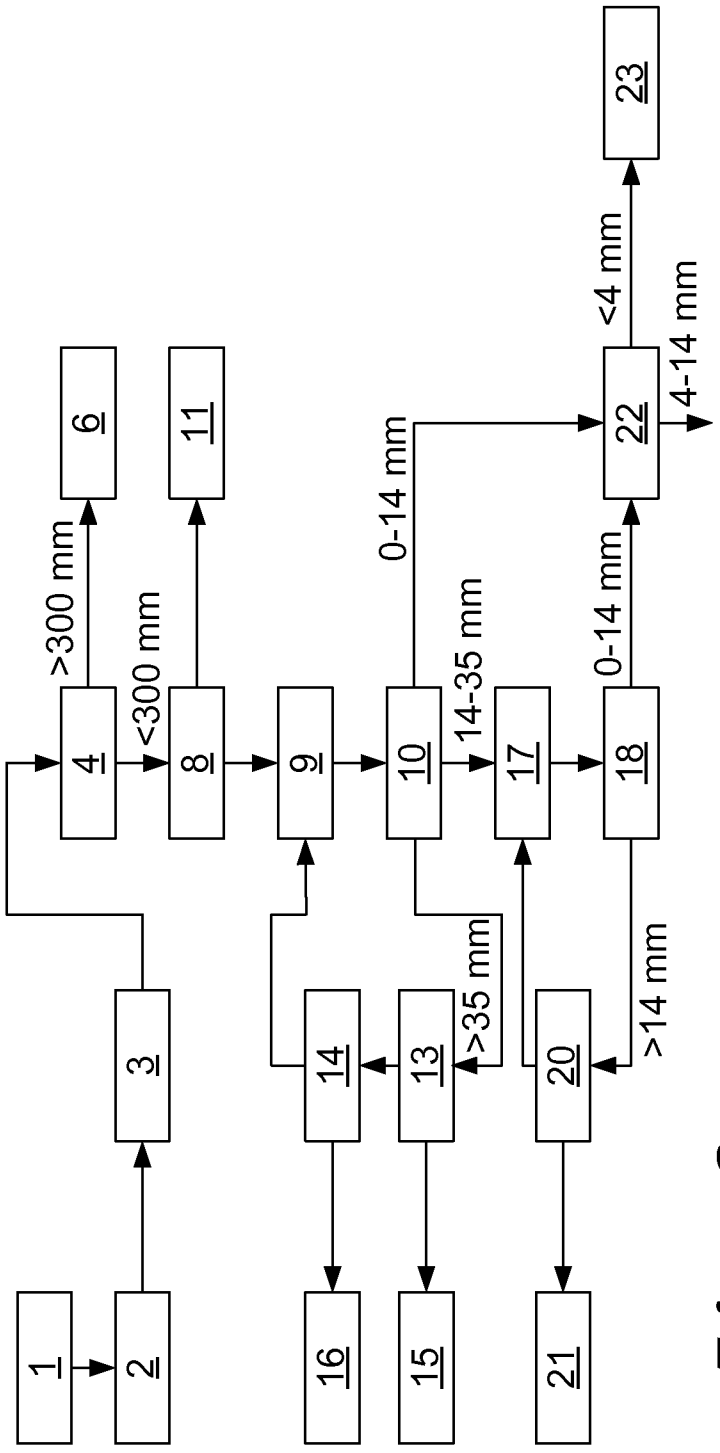

1
2
3
4
6
>300 mm
<300 mm
8
11
9
10
0-14 mm
14-35 mm
17
18
0-14 mm
22
<4 mm
23
4-14 mm
14
13
>35 mm
20
>14 mm
16
15
21

Fig. 2

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2015/078641

A. CLASSIFICATION OF SUBJECT MATTER
INV. C04B28/08 C04B28/26 C04B111/10 C04B111/60
ADD.

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)
C04B

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 practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2012/028419 A1 (NOVACEM LTD [GB]; DEVARAJ AMUTHA RANI [GB]; LEE HAI XIANG [GB]; MARTIN) 8 March 2012 (2012-03-08)	1-22
Y	page 7, paragraphs 1,2; claim 1 page 8, paragraph 2 page 7, last paragraph	23-25
X	DE 30 49 003 A1 (JAPAN PROCESS ENG [JP]) 10 September 1981 (1981-09-10)	1,2,4-9, 16-22
Y	claim 1	23-25
X	IT 1 146 894 B (KI INZH STR INST [SU]) 19 November 1986 (1986-11-19) the whole document	1,2,21

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
9 March 2016	24/03/2016

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Roesky, Rainer

1

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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2015/078641

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	ALTAN YILMAZ ET AL: "Mechanical properties of ferrochromium slag in granular layers of flexible pavements", MATERIALS AND STRUCTURES., vol. 43, no. 3, 1 April 2010 (2010-04-01), pages 309-317, XP055202529, GB ISSN: 1359-5997, DOI: 10.1617/s11527-009-9490-2 the whole document -----	23-25

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2015/078641

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IT 1146894 B	19-11-1986	NONE	