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(54) Particulate refractory compositions for use in the manufacture of foundry moulds and cores, methods of preparing same and corresponding uses

(57) The invention relates to a method of preparing a particulate refractory composition for use in the manufacture of foundry moulds and cores from spent foundry moulds or cores formed of refractory material and an alkaline binder containing alkali metal ions, the method comprising the following steps: providing broken material from spent foundry moulds or cores or preparing broken material from spent foundry moulds or cores, mixing the broken material with an additive comprising or consisting of one or more particulate constituents selected from the group consisting of aluminum hydroxide, synthetic zeolites and natural zeolites and subjecting the mixture to a heat treatment at a temperature in the range of from 400 to 750 °C. Furthermore the invention relates to particulate refractory composition for use in the manufacture of foundry moulds and cores.

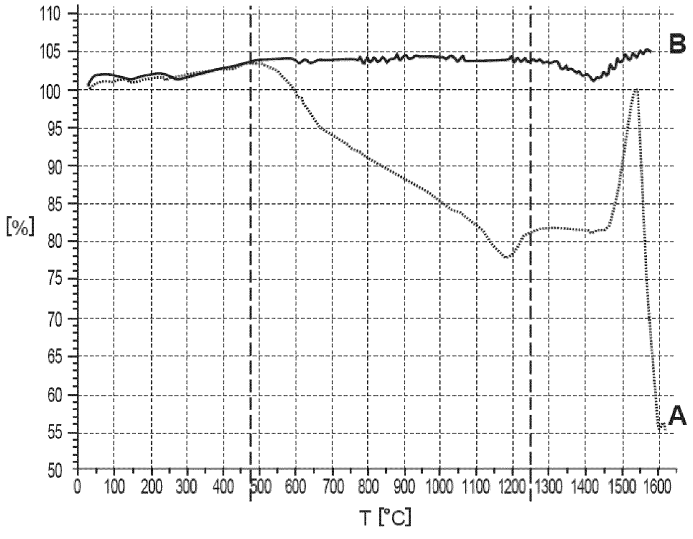

Fig. 1

EP 2 692 460 A1

Description

[0001] The invention relates to particulate refractory compositions for use in the manufacture of foundry moulds and cores, methods of preparing same and corresponding uses.

[0002] More particularly, according to a first aspect, the invention relates to a method of preparing a particulate refractory composition (hereinafter according to the terminology typically used in practice also referred to as "sand") for use in the manufacture of foundry moulds and cores from spent foundry moulds or cores formed of refractory material and an alkaline binder containing alkali metal ions. Even more particularly, the invention relates to a method of preparing a particulate refractory composition (i.e. sand) by reclamation of foundry sands from spent foundry moulds and cores formed of refractory material and an alkaline binder containing alkali metal ions.

[0003] According to a second aspect, the invention relates to a particulate refractory composition for use in the manufacture of foundry moulds and cores, obtainable by a method according to the first aspect of the invention.

[0004] According to a third aspect, the invention relates to a method of making a foundry mould or core, wherein a particulate refractory composition is used which is prepared according to the method of the invention.

[0005] According to a fourth aspect, the invention relates to the use of certain suspensions

(i) for reducing the likelihood of sintering and/or fritting during heat treatment of broken material from spent foundry moulds or cores
and/or

(ii) for removing alkali metal ions from broken material from spent foundry moulds or cores.

[0006] Broken material from spent foundry moulds and cores is a useful starting material according to the present invention, and is in many cases a material fabricated by (i) bonding foundry sand (particulate refractory composition) with a phenolic resin binder in strong alkaline aqueous solution (i.e., an alkaline phenolic resin binder), wherein the binder has been cured with a liquid or gaseous organic ester or with carbon dioxide gas, to give a foundry mould or core, and (ii) breaking said mould or core after use, i.e. breaking the spent foundry mould or core. Since the phenolic resin is typically supplemented with sodium hydroxide and/or potassium hydroxide to obtain the necessary alkalinity the resin is a mixture of organic (phenolic resin) and inorganic (hydroxide) compounds. Alternatively, an alkaline inorganic binder (e.g. (i) modified silicates in combination with inorganic oxides and (ii) water glass binders comprising silicon dioxide and alkali metal oxides in a defined ratio) can be used instead of the alkaline phenolic resin binder, and the inorganic binder is then cured as known in the art (e.g. with carbon dioxide or by heat).

[0007] The use of alkaline phenolic resins for the making of foundry cores and moulds is known for many years. Examples are cold setting processes (so called No-Bake systems) wherein the binder is cured with liquid or gaseous esters. Liquid or gaseous esters are for example di- or triacetin, methyl formate, gamma-butyrolactone, epsilon-caprolactone and propylene carbonate. Other processes comprise binders for core making that are cured by gassing with carbon dioxide. The alkaline phenolic resin binder is usually prepared by mixing phenol and formaldehyde in a defined molar ratio under alkaline conditions. The defined molar ratio (formaldehyde: phenol) typically is in the range of from 1.5 : 1.0 to 2.2 : 1.0. The molar ratio of hydroxide (e.g. potassium hydroxide) and phenol (KOH : phenol) is usually in the range of from 0.2 : 1.0 to 1.2 : 1.0.

[0008] There are several No-Bake systems known for manufacturing foundry moulds and cores comprising alkaline phenolic resin binders. Such foundry moulds and cores can be used in casting processes to finally give (after the respective mould or core has been used) the broken material which is an appropriate starting material for the purposes of the present invention. Broken material from spent foundry moulds or cores, wherein the moulds or cores have been produced according to a No-Bake process, are a useful starting material in methods of the present invention.

[0009] For example, in the so-called Alphaset process (the term alphaset indicating an alkaline phenolic resin cured with an organic ester) highly condensed phenols are solubilized in a sodium hydroxide solution (alternatively in a potassium hydroxide solution or in a mixture thereof). The solvent usually is water and the ratio between alkali metal hydroxide and phenols varies from 0.5 : 1 to 1.2 : 1. In order to cure the resin binder liquid esters are added. The process is described in detail in EP 0 085 512 B1. The amount of hydroxide is for example between 18 and 23 % by weight referred to the dry weight of the composition. Broken material from spent foundry moulds or cores, wherein the moulds or cores have been produced according to the Alphaset process, are a useful starting material in methods of the present invention.

[0010] The so-called Betaset process is similar to the Alphaset process but the ratio between hydroxide and phenols may vary from 0.2 : 1 to 1.2 : 1 and curing of the resin binder is accomplished by gaseous esters (e.g. methyl formate). The process is described in detail in US 4,980,394. The amount of hydroxide is for example between 20 and 25 % by weight referred to the dry weight of the composition. Broken material from spent foundry moulds or cores, wherein the moulds or cores have been produced according to the Betaset process, are a useful starting material in methods of the present invention.

[0011] The curing of a phenolic binder can also be carried out by applying an inorganic curing agent. The use of carbon dioxide is disclosed in US 4,977,209. The amount of hydroxide in such a process is for example 30 % by weight referred to the dry weight of the composition. Broken material from spent foundry moulds or cores, wherein the moulds or cores have been cured with carbon dioxide, are also a useful starting material in methods of the present invention.

[0012] Foundry moulds and cores manufactured according to one of the above mentioned processes have in common that a high amount of alkalinity is present in said mixtures. Advantages of these water-based systems are, next to the competitive binder costs, technological advantages like good collapsibility and a good casting finish as well as low emissions during core and mould making and casting. Disadvantages are that the binders are supplemented with high amounts of hydroxides. This high alkalinity mainly remains in the spent foundry sands after casting, in particular in the form of oxides and hydroxides of alkali metals. Conventional reclamation methods (e.g. mechanical attrition) do not sufficiently remove the alkalinity from said spent foundry sands.

[0013] Washing of the sand to remove soluble alkaline components would be an ideal solution to clean the sand. However, such washing process is not practicable as it would create vast quantities of polluted waste water as well as high energy costs for drying the sand.

[0014] Recently, the interest in alkaline phenolic No-Bake systems has increased since the expenses for carrying out alternative No-Bake systems using furan resins are dramatically fluctuating due to periodic shortages of the main ingredient furfuryl alcohol that is derived from natural resources. The carbon dioxide-cured systems that are used for core making gain importance because of their environmental friendliness compared to solvent containing and amine-cured Urethane cold-box systems.

[0015] Consequently, there is an increasing demand to recycle/reclaim foundry sands (particulate refractory composition for use in the manufacture of foundry moulds and cores) from foundry moulds and/or cores after casting. For environmental and commercial reasons it is desirable to reclaim and reuse as much foundry sand as possible and to remove the high amount of alkalinity in order to save costs on dumping.

[0016] One known conventional method of sand reclamation is a mainly mechanical reclamation and comprises attrition of the bonded sand from spent foundry moulds or cores to break up sand lumps into individual particles. When working with (reclaimed) sand obtained after attrition, the strength of moulds and cores made with ester- or carbon dioxide-cured phenolic resins are generally far inferior compared to the strength obtained with new sand or reclaimed sand from other processes. This is also true for sand obtained from heat-, ester- or CO_2-curing silicate systems (i.e. inorganic systems). Conventional attrition processes allow only a reclamation rate of approximately 70 to 85 % and in practice demand addition of new or otherwise reclaimed sand (e.g. through thermal reclamation at high temperatures) to maintain acceptable performance levels.

[0017] Thus, sand conventionally reclaimed by attrition shows hardly acceptable bonding properties due to the remaining amount of alkalinity and/or organic compounds (resin) on the sand grain surfaces. This effect increases with the number of reclamation cycles, and the binding performance and strength is even further reduced.

[0018] In order to avoid such negative effects as described above additional reclamation processes are applied after mechanical attrition of spent foundry sands. A further step of sand reclamation can involve a heat treatment following the mechanical attrition to completely remove (decompose) all organic impurities and residues. A known technique is to heat the sand in a fluidized bed (further details are provided below in the specification). However, it has been found that especially in the case of alkaline resins, probably due to their high content of alkalinity, heat treatment can lead to agglomeration of the sand grains and preventing the fluidized bed from properly functioning. This negative effect is sometimes described as fritting or sintering of the fluidized bed. This fritting/sintering process is a physicochemical process resulting in the formation of solidified objects which means the fusion or agglomeration of particulated, powdery substances (e. g. sand grains) under increased temperatures. In the context of the present invention, this fritting/sintering process is undesirable and should be avoided.

[0019] It is generally assumed that the high amounts of alkaline metal oxides and hydroxides (e.g. sodium and/or potassium hydroxide and oxide, respectively) react under increased temperatures with fine silica to form glass. This glass covers the surfaces of the sand grains and forms bridges between individual grains that lead to the above described fritting/sintering process (agglomeration). Most importantly, the fritting/sintering dramatically reduces the refractoriness of the substrate.

[0020] A number of patents are known which disclose the addition of various additives that aim to prevent fritting/sintering or to otherwise improve the quality of thermally and/or mechanically reclaimed sand. EP 2 191 908 A1 discloses the use of silicon oils as additives for improved mechanical reclamation of sands. According to own experiments, this additive does not remove the alkalinity and is therefore not ideal.

[0021] EP 0 949 978 B1 discloses the use of carbohydrates as additives added prior to heat treatment to prevent sand grain fusion. However, this method in own experiments proved unsuccessful as no potassium is removed and the potassium content of the reclaimed sand became too high with intensive reuse therefore compromising the rebond strength and refractoriness.

[0022] WO 94/05448 discloses the use of additives like halogen acids, sulphuric acid, boric acid and ammonium salts

of these acids that react with potassium compounds to form salts that have a melting point of at least 550 °C, preferably above 700 °C. The unacceptable disadvantage of this process in own experiments was that a high degree of corrosion was observed in the treatment plants.

[0023] WO 94/26439 discloses the use of particulate active clay additives added prior to the heat treatment. It is disclosed that the strength levels obtained with reclaimed sand are improved and that the level of elutable alkali is dramatically reduced after the reclamation process. However, in own experiments (compare example 3.1) it has been found that with this additive the strength levels drop with each reclamation cycle and was too low to manufacture cores or moulds. Furthermore, EP 1 753 560 B1 discloses that this process suffers from the disadvantage that very fine clay particles are retained with the treated sand with a resultant lack of potassium (or other alkali) removal.

[0024] WO 2005/107975 A1 discloses the use of pozzolanic additives such as volcanic-, fuel-and fly ashes as well as calcined bauxite to reduce fritting/sintering of the fluidized bed of a thermal reclamation unit. A common characteristic of the pozzolanic additives is their content of reactive SiO_2. It is disclosed that the pozzolanic additives react with potassium and are removed after the reclamation process together with the dust. However, it is known and has been confirmed in own experiments that pozzolanic materials have a potential reactivity and that it is therefore difficult to prepare storage-stable suspensions. Another disadvantage is that the pozzolanic additives can be obtained from natural sources or are waste products which can have a varying composition making it more difficult to ensure stable and reproducible process conditions.

[0025] Furthermore, pozzolans contain mostly fine materials and varying amounts of finely divided SiO_2 that, as shown by own experiments (further details are shown in example 4.), has a significant influence on the degree of fritting and glass formation and, therefore, should be avoided.

[0026] A primary object of the present invention is to provide an alternative or improved method of preparing a particulate refractory composition for use in the manufacture of foundry moulds and cores from spent foundry moulds or cores formed of refractory material and an alkaline binder containing alkali metal ions. The method should avoid or at least alleviate at least some problems or disadvantages associated with the prior art methods discussed above.

[0027] According to the present invention this object is achieved by a method of preparing a particulate refractory composition for use in the manufacture of foundry moulds and cores from spent foundry moulds or cores formed of refractory material and an alkaline binder containing alkali metal ions, the method comprising the following steps:

- providing broken material from spent foundry moulds or cores or preparing broken material from spent foundry moulds or cores,
- mixing the broken material with an additive comprising or consisting of one or more particulate constituents selected from the group consisting of aluminium hydroxide, synthetic zeolites and natural zeolites and
- subjecting the mixture to a heat treatment at a temperature in the range of from 400 to 750 °C.

[0028] In the present specification the generic term "zeolites" refers to both and does not distinguish between natural and synthetic zeolites if not stated otherwise. A definition of natural and synthetic zeolites is given below in the specification.

[0029] "Aluminium hydroxide", $Al(OH)_3$, sometimes erroneously called hydrate of alumina (in German: Tonerdehydrat), is found in nature as the mineral gibbsite (monoclinic; also known as hydrargillite) and its three, much more rare polymorphs: bayerite (hexagonal), doyleite and nordstrandite. Closely related are aluminium oxide hydroxide, AlO(OH), differing only by loss of water. These compounds together are the major components of the aluminium ore bauxite. Freshly precipitated aluminium hydroxide forms gels, which is the basis for application of aluminium salts as flocculants in water purification. This gel crystallizes with time.

[0030] The naming for the different forms of aluminium hydroxide is ambiguous and there is no universal standard. All four polymorphisms have a chemical composition of aluminium trihydroxide (an aluminium atom attached to three hydroxide groups).

[0031] Gibbsite is also known as hydrargillite, with gibbsite used most commonly in the United States and hydrargillite used more often in Europe. In 1930 it was referred to as α-alumina trihydrate to contrast it with bayerite which was called β-alumina trihydrate (the alpha and beta designations were used to differentiate the more- and less-common forms respectively). In 1957 a symposia on alumina nomenclature attempted to develop a universal standard, resulting in gibbsite being designated γ-$Al(OH)_3$ and bayerite becoming α-Al(OH)3 and nordstrandite being designated $Al(OH)_3$. Based on their crystallographic properties, a suggested nomenclature and designation is for gibbsite to be α-Al(OH)3, bayerite to be designated β-Al(OH)3 and both nordstrandite and doyleite are designated Al(OH)3. Under this designation, the α and β prefixes refer to hexagonal, close-packed structures and altered or dehydrated polymorphisms respectively, with no differentiation between nordstrandiate and doyleite.

[0032] The term "Aluminium hydroxide" as used in the present text refers to any of the above mentioned different forms of aluminium hydroxide. For preferred forms see below.

[0033] If not indicated otherwise, the term "Aluminium hydroxide" as used in the present text furthermore comprises aluminium oxide hydroxide, AlO(OH), differing from $Al(OH)_3$ only by loss of water. AlO(OH), exists in two forms: α-AlO(OH) (Diaspor) and γ-AlO(OH) (Böhmit). Aluminium hydroxide is capable to form aluminates upon reacting with alkali metal hydroxides.The generic formula of such compounds is $M[Al(OH)_4]$, wherein M means the alkali metal ion.

[0034] It has surprisingly been found that said additive comprising one or more particulate constituents selected from the group consisting of aluminium hydroxide, synthetic zeolites and natural zeolites reduces the likelihood of fritting/sintering of the sand grains and does not disturb the flowability of a fluidized bed in a reclamation unit. Furthermore, said additives do not bind sand particles. The constituents of said additives are typically fully removable from the mixture after heat treatment by dedusting, and along with the dust/fines advantageously a high amount of alkali metal ions (for example potassium ions) can be removed.

[0035] The method according to the invention is preferably a method (as described above), wherein the alkaline binder containing alkali metal ions is an organic binder. Alkaline organic binders are typically prepared by mixing phenol and formaldehyde in defined molar ratios under alkaline conditions to obtain resols (phenol formaldehyde resins). The defined molar ratio (formaldehyde : phenol) typically is in the range of from 1.5 : 1.0 to 2.2 : 1.0. The molar ratio of hydroxide (e.g. potassium hydroxide) and phenol (KOH : phenol) is usually in the range of from 0.2 : 1.0 to 1.2 : 1.0. The resulting alkaline organic resin binders are usually employed in Alphaset, Betaset and CO_2-curing processes (as defined above). The method of the invention and the additives used therein, in particular the additives designated as being preferred, is particularly useful in cleaning the surfaces of particulate material (sand) from such organic binders. The properties of a (cleaned) particulate refractory composition, reclaimed from spent foundry moulds or cores formed of refractory material and an alkaline organic binder containing alkali metal ions are close to the properties of the corresponding virgin particulate refractory composition, i.e. the particulate refractory composition present before first contact with binder. However, in order to improve the bonding strength of new foundry molds and cores the particulate refractory composition, reclaimed from spent foundry moulds or cores can be optionally mixed with virgin particulate refractory composition. Particularly surprising and positive results have been achieved in methods of the present invention wherein the alkaline organic binder (which is to be removed in the reclamation process) is a binder as defined above.

[0036] Alternatively, the method according to the invention is preferably a method (as described above), wherein the alkaline binder containing alkali metal ions is an inorganic binder. In own experiments it has surprisingly been found that the method of the invention and the additives used therein, in particular the additives designated as being preferred, are also useful in cleaning the surfaces of particulate material (sand) from such inorganic binders. The properties of a (cleaned) particulate refractory composition, reclaimed from spent foundry moulds or cores formed of refractory material and an alkaline inorganic binder containing alkali metal ions are improved compared to a particulate refractory composition, reclaimed from spent foundry moulds or cores formed of refractory material and an alkaline inorganic binder containing alkali metal ions not treated according to the method of the invention. Particularly surprising and positive results have been achieved in methods of the present invention wherein the alkaline inorganic binder (which is to be removed in the reclamation process) is usually selected from the group consisting of (i) modified silicates in combination with inorganic oxides and (ii) water glass binders comprising silicon dioxide and alkali metal oxides in a defined molar ratio. The molar ratio of silicon dioxide to e.g. sodium oxide typically is in the range of from 2.3 : 1 to 3.0 : 1. Cores and moulds manufactured with said organic alkaline or inorganic alkaline binders (as defined above) are in most cases excellent starting materials for the method of the invention.

[0037] As shown above, the fritting/sintering during the heat treatment can be reduced by means of the addition of additives comprising one or more particulate constituents selected from the group consisting of aluminium hydroxide, synthetic zeolites and natural zeolites. Thus, according to the invention, the method (as described above, in particular as preferably described) is preferably a method, wherein the amount of constituents in the additive is selected such that sintering and/or fritting is reduced during the heat treatment in comparison with a method not comprising mixing the broken material with an additive but being otherwise identical. In practice, the skilled person will typically conduct a number of simple experiments in order to identify an appropriate amount of constituents in the additive, i.e. the appropriate additive formulation (type and amount of additive constituent), and an appropriate amount of additive, for a given type and amount of spent foundry mould or core. Of course, the appropriate additive and amount of additive will also be determined by the apparatus available for mixing and heat treatment etc. The person skilled in the art knows methods which can be used to verify the appropriate amount and type of constituents in the additive. The concepts of DIN 51730 for example provide a method (Testing of solid fuels - Determination of fusibility of fuel ash) to verify the results achieved with defined amounts and types of constituents in the additive by determining the cross sectional area values of specimens manufactured with heat treated broken material. These cross sectional area values indicate the progress of fritting/sintering in dependence of the temperature (see example 4. and Figure 1). As another example, the skilled person can take pictures of heat treated broken material with an optical microscope to analyse the surfaces of heat treated particles (compare 3.1 under the heading Examples). Such an analysis advantageously shows whether the surfaces are clean

or still covered by remaining binder material. Both methods are suitable to determine the appropriate amount and type of constituents in the additive, in particular for broken material (sand) which has been obtained from spent foundry moulds or cores formed of refractory material and an alkaline binder containing alkali metal ions. An optical analysis using a microscope is a preferred method to analyze sand grain particles and to identify whether and to which extent sintering and/or fritting has occurred (in comparison with a method not comprising mixing the broken material with an additive but being otherwise identical).

[0038] An important parameter of the heat treatment in a method according to the invention is the temperature. The method according to the invention preferably relates to a method (as described above, in particular as designated as being preferred), wherein the heat treatment is at a temperature in the range of from 400 to 750 °C, more preferably 450 to 670 °C, even more preferably 530 to 650 °C, most preferably 580 to 600 °C. The method of the invention and the additives used therein, in particular the additives designated as being preferred, is particularly useful in cleaning the surfaces of broken material (sand) from remaining binder material. This cleaning process is preferably carried out at a temperature between 400 to 750 °C because in this temperature range the heat treatment ensures a complete burning/combustion of the remaining binder. As known to a person skilled in the art, the burning process (this means the quantity of burned/combusted binder material) depends on the type of binder that has been used to manufacture the broken material and the temperature used during heat treatment. The method according to the invention surprisingly showed an excellent burning/combustion of alkaline organic binders (as defined above, in particular as designated as being preferred). Thus, especially preferred methods of the invention relate to a method (as described above, in particular as designated as being preferred) wherein the alkaline binder containing alkali metal ions is an organic binder, and wherein the heat treatment is at a temperature at which the binder is burned/combusted.

[0039] Excellent results have been also observed after heat treatment and dedusting for broken materials obtained from spent moulds and cores comprising alkaline inorganic binders (as defined above, in particular as designated as being preferably). The surfaces of the broken material particles, in particular sand grains, have been advantageously cleaned because any remaining combustible (e.g. organic) parts have been burned/combusted and fines have been removed by means of dedusting.

[0040] Temperatures below 400°C usually (i) do not guarantee a complete burning/combustion of the residual binders (in particular organic binders) during heat treatment and/or (ii) lead to emissions in the exhaust gases due to unburned binder material. These emissions usually comprise volatile organic compounds because at lower temperatures the binder material (e.g. resin) may be removed from the broken material (sand grain surface) by for example vaporization but temperature is insufficient to destroy the binder vapor, which will be passed to the atmosphere. Furthermore, broken material (sand) obtained after heat treatment below 400 °C exhibits insufficient binding properties (which means an insufficient binding strength upon manufacturing moulds and cores with such broken material). On the other hand, temperatures above 750 °C strongly increase the likelihood of fritting/sintering of the broken material during heat treatment.

[0041] The method according to the invention can be carried out in various scales and may e.g. include mixtures (comprising the broken material and an additive comprising or consisting of one or more particulate constituents selected from the group consisting of aluminium hydroxide, synthetic zeolites and natural zeolites) of less than 1 kg (e.g. 500 g) up to 15 tonnes.

[0042] The method according to the invention (as described above, in particular as designated as being preferred) can be carried out as a batch process or as a continuous process. Both processes can be performed in a thermal reclamation unit (this means a thermal reclamation unit particular for sand reclamation) capable of providing suitable temperatures during heat treatment. In most cases, the thermal reclamation unit advantageously provides stable and reproducible treatment conditions during the heat treatment. Continuous operating thermal reclamation units can be (but are not necessarily) part of a thermal reclamation plant which is commercially available (e.g. Richards/Omega Alkaline Phenolic Thermal Sand Reclamation Plant typically comprising a PXG "Phoenix" thermal reclamation unit; Omega Foundry Machinery Ltd.). For example, the Alkaline Phenolic Thermal Sand Reclamation Plant (as commercially offered) is typically made in standard unit sizes from 0.25 tons per hour to 12.0 tons per hour, in increments of 0.25 tons per hour, and is advantageously designed to treat broken material obtained from moulds and cores cured with alkaline phenolic ester type binders. Thus, the method according to the invention (as described above, in particular as designated as being preferred) preferably relates to a method carried out in a thermal reclamation unit, more preferably in a continuous operating thermal reclamation unit.

[0043] In methods according to the invention (as described above, in particular as designated as being preferred) the binder preferably is an alkaline resol phenol-aldehyde resin binder, preferably as used in a method of bonding foundry sand with phenolic resin binder in alkaline aqueous solution, wherein the binder is cured with an liquid or gaseous organic ester or with gaseous carbon dioxide. Such resin binders and corresponding methods of bonding foundry sand with said binders are for example disclosed in EP 0 556 955 B1, EP 0 085 512 B1, US 4,980,394 and US 4,977,209, and broken material from moulds and cores manufactured accordingly are preferred starting materials in methods according to the invention. In the presence of the additive used in the present invention such broken material shows an excellent burning/

combustion of said binders during the heat treatment step (at temperatures as defined above, in particular as designated as being preferred). Fritting and/or sintering is avoided or at least significantly reduced. Another advantage is that costs for dumping spent broken material can be significantly reduced as well as the amount of virgin sand (this means fresh or new sand before first contact with a binder) which is typically added in practice in order to maintain excellent properties of the sand mixture used.

[0044] In the method according to the invention (as described above, in particular as designated as being preferred) the additive preferably comprises its constituents suspended in water. In order to mix the additive with broken material from spent foundry moulds or cores the most practical way is to add the additive as a suspension. One advantage is that a suspension can be accurately and easily dosed. Furthermore, the addition of a suspension prevents dust formation and guarantees homogenous mixing with the substrate. Thus, additives as preferably used in the method according to the invention (as described above, in particular as designated as being preferred) are preferably suspensions of (i) aluminium hydroxide in water or (ii) synthetic zeolites in water or (iii) natural zeolites in water or (iv) mixtures of synthetic and natural zeolites in water or (v) mixtures of aluminium hydroxide and synthetic zeolites in water or (vi) mixtures of aluminium hydroxide and natural zeolites in water or (vii) mixtures of aluminium hydroxide and natural and synthetic zeolites. Furthermore, said suspensions (i) to (vii) are advantageously storage-stable and usually exhibit a defined composition of constituents. This ensures stable and reproducible process conditions in a method according to the invention.

[0045] A suspension of, e.g., aluminium hydroxide in water can be prepared by mixing aluminium hydroxide in water by means of a high-performance mixer. As typical in the art, suspending agents and thickeners are optionally added to the suspension in order to avoid or minimize sedimentation and to improve mixing with the broken material, in particular sand. Zeolites can be added as further active ingredient. Optionally, additional additives (e.g. surfactants) are added to reduce the surface tension of the suspension. The resulting aluminium hydroxide suspension contains a total amount of solid material of about 20 to 70 %, preferably 35 to 55 %, more preferably 40 to 50 % by weight based on the total amount of the suspension. Preferably at least 70 %, preferably at least 75 % by weight, based on the total amount of solid material in the suspension, is natural zeolite.

[0046] Preferably, at least 90 %, preferably at least 95 % by weight, based on the total amount of solid material in the suspension, is selected from the group consisting of aluminium hydroxide and zeolite. It has surprisingly been found that a suspension of natural and/or synthetic zeolites in water likewise shows excellent results, in particular if the suspension is homogeneously mixed with the broken material prior to the heat treatment. A similar positive effect of reducing the likelihood of fritting/sintering as described throughout this specification for the use of aluminium hydroxide, in particular for the use of aluminium hydroxide suspended in water, in the method according to the invention, has been found for the use of natural and/or synthetic zeolites, in particular if natural and/or synthetic zeolites are suspended in water.

[0047] The steps of preparing a suspension of natural and/or synthetic zeolites in water correspond to the steps of preparing a suspension of aluminium hydroxide in water. Thus, the aforementioned aspects concerning the preparation of an aluminium hydroxide suspension do also apply to the preparation of a suspension comprising natural and/or synthetic zeolites. Aluminium hydroxide can be added as further active ingredient. Preferred zeolite suspensions contain a total amount of solid material of about 20 to 60 %, preferably 30 to 50 %, more preferably 35 to 45 % by weight based on the total amount of aluminum hydroxide in the suspension. Preferably, at least 90 %, preferably at least 95 % by weight, based on the total amount of solid material in the suspension, is selected from the group consisting of aluminium hydroxide and zeolite.

[0048] Furthermore, it has been surprisingly found that a suspension of a mixture of aluminium hydroxide and natural and/or synthetic zeolites in water shows equally excellent results if the suspension is homogeneously mixed with the broken material prior to the heat treatment. A similar positive effect of reducing the likelihood of fritting/sintering as described throughout this specification for the use of aluminium hydroxide as well as for the use of zeolites (in particular if said compounds are suspended in water) in the method of the invention, has been found also for the use of a mixture of aluminium hydroxide and natural and/or synthetic zeolites (in particular in aqueous suspensions).

[0049] The steps to prepare a suspension of a mixture of aluminium hydroxide and natural and/or synthetic zeolites in water correspond to the steps of preparing either a suspension of aluminium hydroxide in water or of zeolites in water. Thus, the aforementioned aspects concerning the preparation of an aluminium hydroxide suspension and a zeolite suspension also apply to the preparation of a suspension comprising a mixture of aluminium hydroxide and natural and/or synthetic zeolites.

[0050] In methods according to the invention (as described above, in particular as designated as being preferred) said suspensions are preferably employed for preparing the mixture which is then subjected to heat treatment at a temperature as defined above.

[0051] The method according to the invention relates to a method (as described above, in particular as designated as being preferred), wherein the broken material is mixed with an additive comprising aluminium hydroxide and/or one or both of synthetic zeolites and natural zeolites. In order to achieve a decrease of the likelihood of fritting/sintering of broken material (in particular sand) at least one constituent of an additive as used in a method according to the invention

is mixed with said broken material. However, a mixture of preferred constituents in a suspension advantageously decreases even more the likelihood of fritting/sintering of the broken material (in particular sand) during heat treatment compared to broken material mixed with a suspension comprising either aluminium hydroxide or natural and/or synthetic zeolites.

[0052] The mixing of broken material and additive according to the method of the invention can be for example performed in a thermal reclamation plant (see above). Such a thermal reclamation plant provides excellent results when employed in the method of the invention. However, said mixing can be also performed in a separate step in other typical mixing units as known to the skilled person, and the resulting mixture can subsequently be subjected to heat treatment in a thermal reclamation unit

[0053] In the method according to the invention (as described above, in particular as designated as being preferred), the mixture simultaneously with being subjected to said heat treatment is preferably fluidized in a fluidized bed apparatus or moved (preferably mixed) in a thermal sand reclamation unit. As mentioned above, the heat treatment of the mixture in a method according to the invention leads to the burning/combustion of remaining binder material. It is therefore preferred that the mixture is stirred up or moved in order to improve the effects of the heat treatment. For this purpose the heat treatment in the method according to the invention is more preferably carried out using fluidization of the mixture in a fluidized bed or movement (mixing movement) in a thermal sand reclamation unit such as a rotary reclamation apparatus. A rotary reclamation apparatus is for example disclosed in US 6,286,580 B1. Fluidization of the mixture in the method according to the invention is more preferably achieved in a thermal reclamation unit or a thermal reclamation plant (as described above). The skilled person is familiar with the appropriate conditions in order to carry out such heat treatment step.

[0054] In a method according to the invention (as described above, in particular as designated as being preferred), solid matter (preferably dust and fines) containing alkali metal ions is preferably removed from the mixture during and/or after the heat treatment, so that the concentration of alkali metal ions in the remaining mixture decreases. The process of removing solid matters preferably separates the mixture in at least two fractions: (i) a sand fraction comprising the desired heat treated (broken) material and (ii) dust and fines which comprise alkali metal ions and reaction products of constituents of the additives with alkali metal ions. Thus, a preferred removing step is a dedusting step carried out to remove dust and fines. Dust and fines can be removed for example by using a sieve with a defined mesh size. Such a dedusting step using a sieve is preferably used if the method according to the invention is carried out in small scales (e.g. laboratory scales). However, e.g. when the method according to the invention is carried out in a thermal reclamation unit (see above) dedusting can be advantageously combined with the use of a fluidized bed. In a fluidized bed the mixture behaves as a fluid. A characteristic of a fluidized bed is that an object with a higher density than the bed will sink, whereas an object with a lower density than the bed will float. This property can be increased by applying a negative pressure to the fluidized bed. Such a fluidized bed allows the removal of dust and fines of lower density (dedusting), and its use is therefore preferred in the method of the present invention. A dedusting step to remove dust and fines which contain alkali metal ions can be carried out during and/or after the heat treatment. Said alkali metal ions are effectively removed, probably because constituents in the additives used in the method according to the invention advantageously react and bind alkali metal ions (in particular potassium ions) and form compounds which are thermally more stable in the temperature range applied to the fluidized bed. The formation of such thermally stable compounds prevents fritting/sintering of the fluidized bed, and said compounds can be removed by dedusting. Thus, dedusting during and/or after heat treatment (as described above) effectively decreases the concentration of alkali metal ions in the mixture. Dedusting can be for example carried out in a thermal reclamation unit (as well as in a thermal reclamation plant) (see above) in combination with a filter unit appropriate to remove dust and fines.

[0055] Thus, in preferred methods according to the invention (as described above, in particular as designated as being preferred), said solid matter (dust and fines) comprises particulate constituents of said additive and/or reaction products thereof. The amount of alkali metal ions may vary and depend on the specific broken materials. As a consequence, the amount of constituents in the additive may not fully react with the alkali metal ions and residual amounts of constituents may remain in the mixture. These remaining constituents are preferably removed during dedusting. In a preferred dedusting step remaining additive constituents are fully removed. However, in case that upon dedusting the constituents aluminium hydroxide and/or zeolites are not fully removed (e.g. due to improper or incomplete dedusting) the total amount of said remaining constituents aluminium hydroxide and zeolites does preferably not exceed 10% by weight based on the total amount of aluminium hydroxide and zeolites comprised in the additive mixed with the broken material.

[0056] In the method according to the invention (as described above, in particular as designated as being preferred), the additive preferably comprises one or more particulate constituents selected from the group consisting of
amorphous aluminium hydroxide ($Al(OH)_3$), monoclinic aluminium hydroxide ($Al(OH)_3$), and hexagonal aluminium hydroxide ($Al(OH)_3$),
synthetic zeolites selected from the group consisting of synthetic mordenite, zeolite A, zeolite L, zeolite X, zeolite Y, ZM5 and ZSM11, and (other) zeolites of the pentasil family of zeolites,
natural zeolites selected from the group consisting of analcime, barrerite, chabazite, brewsterite, clinoptilolite, edingtonite,

erionite, ferrierite, gismondine, gmelinite, gonnardite, harmotome, heulandite, laumontite, levynite, mesolite, mordenite, natrolite, paulingite, pentasil, phillipsite, pollucite, scolecite, stellerite, stilbite and wairakite.

[0057] Natural zeolites which can be employed in the method of the present invention are crystalline and naturally occurring alumosilicates. So far, there are 48 natural zeolites known. Zeolite minerals have been created through hydrothermal conversion of volcanic glasses and tuff-containing sediments, respectively.

[0058] Natural zeolites are for example analcime, barrerite, chabazite, brewsterite, clinoptilolite, edingtonite, erionite, ferrierite, gismondine, gmelinite, gonnardite, harmotome, heulandite, laumontite, levynite, mesolite, mordenite, natrolite, paulingite, pentasil, phillipsite, pollucite, scolecite, stellerite, stilbite and wairakite.

[0059] Synthetic zeolites which can be employed in the method of the present invention are compounds of the formula $M_{2/z}O\ Al_2O_3\ xSiO_2\ yH_2O$, wherein M means a mono- or bivalent metal ions (preferably alkali or alkaline earth metal ions), hydrogen (H) or ammonium ions (NH_4^+). Z represents the atomicy of the cation and x = 1,8 to approximately 12 and y = 0 to approximately 8. There are approximately 150 synthetic zeolites known today which are modifiable based on the incorporation or exchange of foreign atoms during synthesis. Synthetic zeolites originate from SiO_2-containing (e.g. water glass (or liquid glass), silicic acid-bulking agents, colloidal silica) and Al_2O_3-containing (e.g. aluminium hydroxide, aluminates, kaolinite) compounds which react together with alkali hydroxides (e.g. sodium hydroxide) at temperatures > 50 °C in an aqueous phase and finally form crystalline zeolithes.

[0060] Synthetic zeolites are for example synthetic mordenite, zeolite A, zeolite L, zeolite X, zeolite Y, ZM5, ZSM11, and (other) zeolites of the pentasil family of zeolites.

[0061] Preferably, the additive used in the method of the invention is free of puzzolanic constituents such as natural pozzolans occurring in volcanic ash and in volcanic tuff and synthetic pozzolanes, such as pulverized fuel ash, fly ash, gound granulated blast-furnace slag, condensed silica fume, amorphous silica and calcined bauxite.

[0062] Further preferably, the additive used in the method of the invention is free of free reactive silicon dioxide. According to own experiments (compare experiment 4.) the presence of reactive silicon dioxide (SiO_2) strongly favors fritting/sintering of the broken material. Reactive silicon dioxide (SiO_2) in particular is finely divided silicon dioxide providing a large surface area and, thus, an increased reactivity.

[0063] Natural and synthetic zeolites have in common that they exhibit a cation exchange capacity. The cations, compensating the negative charges of the AlO_4-tetraeder, are floating in the hydrated lattice and therefore, are easily exchangeable

against other cations. Hence, zeolites are capable to exchange alkali metal ions in an aqueous solution against other cations. On the basis of their porous structure zeolites can adsorb other molecules. A typical characteristic of zeolites is that they can release water molecules without modifying their crystal structure.

[0064] In the method according to the invention the additives comprise particulate constituents. Preferably, at least a part of the particulate constituents of the additive passes a screen (according to DIN ISO 3310) having a mesh size of 125μm.More preferably, at least a part (preferably at least 80 to 90 % by weight, more preferably 95 % by weight based on the total amount of said constituents) of the particulate constituents selected from the group consisting of aluminium hydroxide (as defined above), synthetic zeolites (as defined above) and natural zeolites (as defined above) passes a screen (according to DIN ISO 3310) having a mesh size of 125μm., which means that at least a part of aluminium hydroxide passes a screen (according to DIN ISO 3310) having a mesh size of 125μm.and/or at least a part of synthetic zeolites passes a screen (according to DIN ISO 3310) having a mesh size of 125μm. and/or at least a part of natural zeolites has passes a screen (according to DIN ISO 3310) having a mesh size of 125μm.. The analysis is preferably conducted according to DIN 66165 or a method of similar relevance and accuracy.

[0065] Particulate constituents (as defined above, in particular as defined as preferably) preferably show an excellent reactivity with alkaline metal ions in the mixture according to the method of the invention and said particulate constituents which have not been reacted with said metal ions can be in most cases advantageously removed by dedusting. Particulate constituents exhibiting a particle size not passing a mesh size of less than 125 μm (the particle size is too large) show disadvantages during the dedusting process. In particular, such particulate constituents disadvantageously show an increased tendency to remain in the heat treated mixture and have a relatively small surface area available for reaction with alkaline materials to be removed from the broken material from spent foundry moulds or cores.

[0066] A further important parameter during heat treatment of the mixture in the method according to the invention is the amount of additive to be used in the mixture. In methods according to the invention (as described above, in particular as designated as being preferred), the total amount of aluminium hydroxide, synthetic zeolites and natural zeolites in the mixture is preferably in the range of from 0.1 to 3 % by weight based on the total weight of broken material, aluminium hydroxide, synthetic zeolites and natural zeolites. This concentration range is preferred to ensure an excellent ratio between said constituents and alkali metal ions. A concentration of less than 0.1 % by weight does in some cases not suffice (i) to decrease the likelihood of fritting/sintering of the broken material and (ii) to significantly decrease the concentration of alkali metal ions in the mixture. A concentration above 3 % by weight in some cases leads to a concentration of constituents in the mixture which cannot sufficiently be decreased by dedusting during or after heat treatment. According to own experiments particularly excellent results have been achieved when the total amount of aluminium

hydroxide, synthetic zeolites and natural zeolites in the mixture is in the range of from 2.0 to 3.0 % by weight based on the total weight of broken material, aluminium hydroxide, synthetic zeolites and natural zeolites.

[0067] A further important parameter is the period of time for subjecting the mixture to heat treatment. The method according to the invention preferably relates to a method (as described above, in particular as designated as being preferred), wherein the mixture is subjected to said heat treatment for a period of from 20 minutes to 12 hours, preferably from 15 minutes to 30 minutes. The period (dwell time) of preferably from 20 minutes to 12 hours, more preferably from 15 minutes to 30 minutes affects the quality of the burning/combustion of remaining binder material. Even at sufficient temperatures (as defined above, in particular as designated as being preferred) the combustion of remaining binder material may be incomplete if the dwell time is too short. On the contrary, if the dwell time is longer than preferred the yield per time is decreased and energy costs for the heat treatment increase. In methods of the invention the use of a thermal reclamation unit (as defined above) is preferred. Such a unit typically provides a 15 minutes bed residence time while the broken material (sand) is subjected to heat treatment in a fluidized bed. A residence time of from 10 to 30 minutes is generally preferred.

[0068] In own experiments it has been found that the method of the invention allows for the preparation of an excellent particulate refractory composition for use in the manufacture of foundry moulds and cores from spent foundry moulds or cores in particular if the measures discussed above regarding the important parameters (temperature, concentration and dwell time; all parameters as defined above, in particular as designated as being preferred) are combined. Thus, in the method of the invention preferably (i) the heat treatment is carried out at temperatures as defined above (in particular as designated as being preferred) and/or (preferably "and") (ii) the total amount of aluminium hydroxide, synthetic zeolites and natural zeolites in the mixture is in the range of from 0.1 to 3 % by weight, preferably in the range of from 2.0 to 3.0 % by weight based on the total weight of broken material, aluminium hydroxide, synthetic zeolites and natural zeolites and/or (preferably "and") (iii) the mixture is subjected to said heat treatment for a period of from 20 minutes to 12 hours, preferably from 15 minutes to 30 minutes.

[0069] According to another aspect the invention relates to a particulate refractory composition for use in the manufacture of foundry moulds and cores, obtainable by a method (as described above, in particular as designated as being preferred) according to the invention. Such a composition can be advantageously obtained if in the method of the invention a thermal reclamation unit (as defined above) is used for the heat treatment step.

[0070] Particulate refractory compositions according to the invention (as described above, in particular as designated as being preferred), in many cases comprise one or more particulate constituents selected from the group consisting of aluminium hydroxide, synthetic zeolites, natural zeolites, and reaction products of alkali oxides with aluminium hydroxide, synthetic zeolites and/or natural zeolites.

[0071] As discussed above, the method of the invention (as described above, in particular as designated as being preferred) preferably comprises a dedusting step to remove solid matters. Dedusting in particular relates to so-called "fines", i.e. to solid particles passing a 0,075 mm (75 μm) sieve, preferably a 0,125mm (125μm) sieve. However, in particular if such a dedusting step is not conducted at all or not conducted properly or completely, a particulate refractory composition of the invention contains dust and fines.

[0072] Said fines usually comprise remaining constituents (e.g. as aluminium hydroxide and/or zeolites) and/or reaction products thereof with alkali metal ions (as described above).

[0073] Preferably, the particulate refractory compositions for use in the manufacture of foundry moulds and cores according to the invention do not comprise aluminium-containing oxy anions.

[0074] According to a further aspect of the invention, the present invention relates to a method of making a foundry mould or core comprising the following steps:

- preparing a particulate refractory composition according to the method of the invention (as described above, in particular as designated as being preferred) or providing a particulate refractory composition for use in the manufacture of foundry moulds and cores, obtainable by a method according to the invention (i.e. a particulate refractory composition of the present invention, as described above, in particular as designated as being preferred)

- mixing the particulate refractory composition with a binder

- shaping the resulting mixture, and

- curing the binder in said shaped mixture.

[0075] In own experiments it has been found that foundry moulds and cores manufactured by using particulate refractory composition from spent foundry moulds or cores exhibit an excellent binding strength (further details can be seen in the example section). The binder used in the method of making a foundry mould or core according to the invention is preferably a binder as discussed above. For example, alkaline organic binders are typically prepared by mixing phenol

and formaldehyde in defined molar ratios under alkaline conditions to obtain resols (phenol formaldehyde resins). The defined molar ratio (formaldehyde : phenol) typically is in the range of from 1.5 : 1.0 to 2.2 : 1.0. The molar ratio of hydroxide (e.g. potassium hydroxide) and phenol (KOH : phenol) is usually in the range of from 0.2 : 1.0 to 1.2 : 1.0. Typical alkaline inorganic binders are (i) modified silicates in combination with inorganic oxides or (ii) water glass binders comprising silicon dioxide and alkali metal oxides in a defined molar ratio. The molar ratio of silicon dioxide to e.g. sodium oxide typically is in the range of from 2.3 : 1 to 3.0 : 1.

[0076] In the method of making a foundry mould or core according to the invention (as described before), the binder is preferably cured with a liquid or gaseous organic ester or with gaseous carbon dioxide. Liquid or gaseous esters are for example di- or triacetin, methyl formate, gamma-butyrolactone, epsilon-caprolactone and propylene carbonate. Foundry moulds or cores manufactured according to the method of the invention advantageously show excellent properties in the foundry and casting processes, and after use they can be recycled as discussed above. I.e., spent foundry moulds or cores manufactured according to the method of the invention can be broken, and the resulting broken material can be used as starting material in a method of the present invention of preparing a particulate refractory composition for use in the manufacture of foundry moulds and cores.

[0077] In another aspect of the invention, the invention relates to the use of a suspension comprising one or more particulate constituents selected from the group consisting of aluminium hydroxide, synthetic zeolites and natural zeolites

(i) for reducing the likelihood of sintering and/or fritting during heat treatment at a temperature in the range of from 400 to 750 °C of broken material from spent foundry moulds or cores
and/or

(ii) for removing alkali metal ions from broken material from spent foundry moulds or cores.

[0078] The person skilled in the art knows how to determine the extent of fritting/sintering caused by heat treatment (i) in a method of the present invention and (ii) in methods known in the art. Examples are mentioned above (e.g. method, following the concepts of DIN 51730, preferred for the purposes of the present invention, or by taking pictures with an optical microscope). The skilled person is also familiar with methods in order to determine the removal of alkali metal ions and/or to determine the concentration of alkali metal ions before and after treatment of the broken material. A method for determining the potassium removal rate (PRR) is disclosed in the example section herein below.

[0079] The invention will be illustrated by the following Examples.

Examples:

Example 1: Additive preparation and additive composition

[0080] Three different additives "Additive A", "Additive B", and "Additive C" (as suspensions) were prepared:

"Additive A" is a suspension of 50 % by weight of aluminium hydroxide in water, based on the total amount of the suspension. The particle size of the aluminium hydroxide is in the range of from 45 μm to 150 μm for 75 % by weight of the total amount of aluminium hydroxide in the suspension.

"Additive B" is an aqueous suspension of 38 % by weight of a mineral mixture, based on the total amount of the suspension, wherein the mineral mixture comprises > 85 % by weight of the natural zeolite clinoptilolite, based on the total amount of the mineral mixture. The particle size of the mineral mixture is, according to the supplier, in the range of from 30 to 100 μm for 30 to 50% by weight of the total amount of the mineral mixture, and the mineral mixture has a total cation exchange capacity of 1,2 to 1,45 mol/kg.

"Additive C" is a 1:1 mixture (by weight) of "Additive A" and "Additive B".

[0081] "Additive A", "Additive B", and "Additive C" were prepared as known to one skilled in the art. This includes mixing of the respective materials (aluminium hydroxide and/or zeolite; water) with common suspension additives such as suspension agents, wetting agents and thickeners. Significant characteristics of "Additive A", "Additive B", and "Additive C" are summarized in Table 1.

Table 1

	"Additive A" (aluminium hydroxide)	"Additive B" (zeolite)	"Additive C" (aluminium hydroxide and zeolite)
Solid content [% by weight] (5-7 g are dried for 10 min. @ 160°C)	52	38	44
Specific gravity [g/ml]	1,44	1,28	1,36
Viscosity, Ford cup 4 mm [s]	19	19	19
Viscosity, Ford cup 6 mm [s]	7,2	6,8	7,2
pH	9,2	8,8	8,9
Color	white-beige	greenish	green

Example 2: Pilot plant trials

[0082] Pilot plant trials were carried out in a Richards/Omega thermal pilot plant. The pilot trials were carried out as follows:

I) A total amount of 1500 kg of broken material (mechanically reclaimed foundry sand) from a No-Bake process (a Resol-Ester process) were split into 3 samples of 500 kg each.

II) Each individual additive ("Additive A", "Additive B" and "Additive C") was prepared according to "Example 1: Additive preparation and additive composition".

III) Three test samples labelled "Test sample A", "Test sample B" and "Test sample C" were prepared as follows using the broken material of step I) and "Additive A", "Additive B" and "Additive C" of step II):

- mixing of 500 kg (for each sample) of the broken material (mechanically reclaimed foundry sand (according to step I)) with 2 % by weight (based on the amount of broken material) of the respective "Additive A", "Additive B" or "Additive C" (in several steps, with a 60 kg batch mixer; mixing time 5 minutes)

After mixing, the resulting mixtures contain (i) broken material (mechanically reclaimed foundry sand) and (ii) the following amounts of particulate constituents, based on the total amount of broken material (sand):

- "Test sample A": approximately 1 % by weight of aluminium hydroxide (from Additive A)
- "Test sample B": approximately 0,7 % by weight of zeolites (from Additive B)
- "Test sample C": approximately 0,9 % by weight of a mixture of aluminium hydroxide and zeolites (from Additive C)

IV) "Test sample A", "Test sample B" and "Test sample C", respectively, were charged into a preheated Richards/Omega thermal plant with an addition rate of approximately 80 kg/h to prepare a particulate refractory composition. The operating temperature was adjusted to 580 to 600 °C and the discharge rate was also approximately 80 kg/h. Dust was removed continuously with a Richards/Omega bag filter unit.
During the heat treatment the fluidized bed of each test sample ("Test sample A", "Test sample B" and "Test sample C") was continuously monitored for signs of fritting/sintering. No such fritting/sintering was observed for said test samples during a continuous process of 8 hours.

V) Determination of the LOI (Loss on ignition) for each sample obtained in step IV). LOI measurements are measurements used in inorganic, analytical chemistry involving the strong heating of a sample to allow volatile substances to escape, until its mass ceases to change. The mass of a sample is determined before and after the heating process to determine the mass difference, which indicates the amount of organic compounds remaining in the broken material

after heat treatment. For this purpose a small amount of the particulate refractory composition was subjected to the measurement and the weight was compared to the weight prior to heat treatment.
LOI measurements showed a LOI of 0,01 to 0,03 %. This proved that the heat treatment excellently removed organic matters.

VI) Preparing the following five samples (sand-mixtures), as defined below, for manufacturing foundry moulds and/or specimens:

- "Test sample A-I" comprising the particulate refractory composition obtained from the broken material of "Test sample A" after step IV),
- "Test sample B-I" comprising the particulate refractory composition obtained from the broken material of "Test sample B" after step IV),
- "Test sample C-I" comprising the particulate refractory composition obtained from the broken material of "Test sample C" after step IV),
- "Reference sample New sand" comprising fresh (virgin) foundry sand (Silica sand),
- "Reference sample Mechanically reclaimed sand" comprising broken material (mechanically reclaimed foundry sand) obtained from a No-Bake process (Resol-Ester process), as provided in step I), above,

by conducting the following steps:

- in a first step mixing for 45 seconds (individually, for the preparation of each sample) the particulate refractory composition obtained from the broken material of the respective test sample after step IV), the fresh (virgin) foundry sand, and the broken material (mechanically reclaimed foundry sand), respectively, with 0.3 % by weight of triacetine, based on the total amount of the particulate refractory composition, the fresh (virgin) foundry sand, and the broken material (mechanically reclaimed foundry sand), respectively,
  and
- in a second step, mixing (each sample) for 60 seconds the resultant mixtures as obtained in the first step with 1.2 % by weight of an alkaline phenol/formaldehyde no-bake binder (Sinotherm 8426, Huettenes-Albertus, Chemische Werke GmbH), based on the total amount of the particulate refractory composition, the fresh (virgin) foundry sand, and the broken material (mechanically reclaimed foundry sand), respectively.

VII) Splitting each sample obtained in step VI) in (i) a minor part and (ii) a major part, wherein the minor part (i) was 1 kg and was used for manufacturing transverse strength test specimens (see step XI), below), and wherein the major part was the remaining part of the sample

VIII) Manufacturing foundry moulds with the major part of "Test sample A-I", "Test sample B-I" and "Test sample C-I" obtained in step VII) using a No-Bake process (Resol-Ester process)

IX) Using the foundry moulds obtained in step VIII) for casting processes

X) Collecting the used (spent) foundry moulds obtained in step IX) of "Test sample A-I", "Test sample B-I" and "Test sample C-I", and mechanical attrition (mechanical reclamation) of said moulds to obtain the respective broken material (mechanically reclaimed foundry sand) from spent foundry moulds used in a No-Bake process (Resol-Ester process)

XI) Manufacturing transverse strength test specimens using the minor part (1 kg) of each sample obtained in step VII) for transverse strength tests carried out with a +GF+ transverse strength tester ("Georg Fischer") according to specification note P 72 (VDG — Merkblatt). For this purpose, the respective 1 kg of each sample was used to manufacture seven +GF+ transverse strength test specimens (tensile strength test pieces) from each sample (i.e. seven specimens of "Test sample A-I", seven specimens of "Test sample B-I", seven specimens of "Test sample C-I", seven specimens of "Reference sample New sand" and seven specimens of "Reference sample Mechanically reclaimed sand"). The transverse strength test measurements were carried out after 1 hour (3 specimens of each sample were tested) and 4 hours (4 specimens of each sample were tested). The results are shown in Table 2.

XII) In a second cycle, steps I) to XI) were repeated, except that (i) no reference samples were prepared in this second cycle and that (ii) in step I) of this second cycle the broken material of "Test sample A-I", "Test sample B-I" and "Test sample C-I" (as obtained in step X) of the first cycle) was used.

[0083] Test samples obtained in step VI) of the second cycle are labeled as follows:

- "Test sample A-II" comprising the respective particulate refractory composition obtained in the second cycle after step IV),
- "Test sample B-II" comprising the respective particulate refractory composition obtained in the second cycle after step IV),
- "Test sample C-II" comprising the respective particulate refractory composition obtained in the second cycle after step IV).

Table 2: Results of transverse strength tests in [N/cm^2] after 1 and 4 hours (after the first and second cycle, see step XI), above)

"Reference sample New sand"		**"Reference sample Mechanically reclaimed sand"**		**"Test samples"**	**First cycle**		**"Test samples"**	**Second cycle**	
1h	4h	1h	4h		1h	4h		1h	4h
108	165	22	45	**"A-I"**	107	196	**"A-II"**	118	186
				"B-I"	97	164	**"B-II"**	97	166
				"C-I"	107	206	**"C-II"**	117	183

[0084] In Table 2 the results of the transverse strength level tests are shown for the specimens of the "Reference sample New sand", "Reference sample Mechanically reclaimed sand" and the three test samples "Test sample A-I", "Test sample B-I", "Test sample C-I" obtained in the first cycle as well as for the three test samples "Test sample A-II", "Test sample B-II", "Test sample C-II" obtained in the second cycle. Values obtained for the "Reference sample New sand" indicate excellent transverse strength levels. Transverse strength levels below values obtained from the "Reference sample New sand" indicate a decreased binding strength. The results show that a particulate refractory composition prepared from spent foundry moulds or cores according to the present invention (Test samples A-I, B-I, C-I, A-II, B-II, C-II) exhibits increased transverse strength levels compared to the transverse strength levels of the "Reference sample Mechanically reclaimed sand". Furthermore, compared to the transverse strength levels obtained from the "Reference sample New sand" the transverse strength levels of the "Test samples" (A-I, B-I, C-I, A-II, B-II, C-II) are at least very similar or even slightly increased after 4 hours.

[0085] Note: In foundry practice it is preferred to add a certain amount of fresh (not recycled) sand in each cycle. In the present pilot plant trials no fresh sand was added.

Example 3: Laboratory trials

Example 3.1: Resol-Ester process

[0086] Three laboratory samples "Laboratory sample A", "Laboratory sample B" and "Laboratory sample C" and two reference samples "Reference sample Pozzolan" and "Reference sample Clay" were prepared by the following steps a), b) and c):

a) providing 3 kg (3 kg for each laboratory sample and 3 kg for each reference sample) of broken material (mechanically reclaimed foundry sand) from spent moulds and cores manufactured by the Resol-Ester process

b) providing three additives ("Additive A", "Additive B" and "Additive C") according to "Example 1: Additive preparation and additive composition" and two reference additives "Additive Pozzolan" and "Additive Clay":

"Additive Pozzolan": Is an aqueous suspension of 40 % by weight of a commercially available pozzolan (pul-

verized fuel ash according to BS 3892 part I) as described in PCT/GB 2005/001482 based on the total amount of the suspension "Additive Clay": Is an aqueous suspension of 30 % by weight of a a thermally treated Kaolin clay commercially available clay based on the total amount of the suspension as described in WO94/26439

c) mixing the broken material provided for each sample (each laboratory sample and each reference sample) with 2 % by weight of the respective Additive (see step b)) based on the total amount of broken material, for 60 seconds with a laboratory mixer, resulting in the above mentioned "Laboratory sample A", "Laboratory sample B", "Laboratory sample C", "Reference sample Pozzolan" and "Reference sample Clay", comprising:

- "Laboratory sample A": broken material and approximately 1 % by weight of aluminium hydroxide (from "Additive A"), based on the total amount of broken material,
- "Laboratory sample B": broken material and approximately 0,7 % by weight of zeolite (from "Additive B"), based on the total amount of broken material,
- "Laboratory sample C": broken material and approximately 0,9 % by weight of a mixture of aluminium hydroxide and zeolite (from "Additive C"), based on the total amount of broken material,
- "Reference sample Pozzolan": broken material and approximately 40 % by weight of commercially available pozzolan (from "Additive Pozzolan"), based on the total amount of broken material,
- "Reference sample Clay": broken material and approximately 30 % by weight of commercially available clay (from "Additive Clay"), based on the total amount of broken material.

[0087] The samples prepared in steps a), b) and c) were then subject to further treatment:

d) heat treatment of each sample obtained in step c) in a muffle furnace (Nabertherm L15/11) at 625 °C for 45 minutes

e) (i) after step d), cooling of each sample to a temperature below 40 °C to obtain a particulate refractory composition of each sample and (ii) homogenization of each particulate refractory composition by mixing each particulate refractory composition for 30 seconds with a laboratory mixer

f) (i) dedusting, i.e. removing dust/fines from each particulate refractory composition obtained in step e) by screening each particulate refractory composition over a 125 μm sieve to obtain a dustless, particulate refractory composition of each sample as well as a corresponding dust fraction and (ii) determination of the quantity and potassium content of the dust (see below "Determination of the quantity and potassium content of the dust") and (iii) determination of the conductivity and the pH of the dustless, particulate refractory compositions (see below "Conductivity, pH and acid demand")

g) preparing the following five samples (sand-mixtures), as defined below, for manufacturing transverse strength test specimens:

- "Laboratory sample A-I" comprising dustless, particulate refractory composi tion obtained from "Laboratory sample A" after step f),
- "Laboratory sample B-I" comprising dustless, particulate refractory composiion obtained from "Laboratory sample B" after step f),
- "Laboratory sample C-I" comprising dustless, particulate refractory composition obtained from "Laboratory sample C" after step f),
- "Reference sample Pozzolan I" comprising dustless, particulate refractory com-position obtained from "Reference sample Pozzolan" after step f),
- "Reference sample Clay I" comprising dustless, particulate refractory composition obtained from "Reference sample Clay" after step f),

by conducting the following steps:

- in a first preparation step, homogenization of each dustless, particulate refractory composition obtained in step f), and

- in a subsequent second preparation step, mixing for 45 seconds each homoge-nized, dustless particulate refractory composition with 0.3 % by weight of triacetine, based on the total amount of the respective homogenized, dustless particulate refractory composition,
and

- in a subsequent third preparation step, mixing for 60 seconds each homogenized, triacetine-containing, dustless, particulate refractory composition with 1.2 % by weight of an alkaline phenol/formaldehyde no bake binder (Sinotherm 8426, Hüttenes-Albertus, Chemische Werke GmbH), based on the total amount of the respective homogenized, dustless particulate refractory composition.

h) splitting each sample obtained in step g) in (i) a minor part of 1 kg and (ii) a major part of 2 kg (the major part of each sample was cured and subsequently mechanically reclaimed).

i) manufacturing transverse strength test specimens using the minor part (1 kg) of each sample as obtained in step h) for transverse strength tests carried out with a +GF+ transverse strength tester ("Georg Fischer") according to specification note P 72 (VDG — Merkblatt). For this purpose, the respective minor part (1 kg) of each sample was used to manufacture seven +GF+ transverse strength test specimens (tensile strength test pieces; i.e. seven specimens of "Laboratory sample A-I", seven specimens of "Laboratory sample B-I", seven specimens of "Laboratory sample C-I", seven specimens of "Reference sample Pozzolan I" and seven specimens of "Reference sample Clay I"). The transverse strength test measurements were carried out after 1 hour (3 specimens of each sample were tested) and 4 hours (4 specimens of each sample were tested). The results are summarized in Table 5.

j) subsequently, collecting the seven measured (i.e. broken in the transverse strength test) test specimens of each sample as obtained in step i) and subjecting said collected specimens to a heat treatment at 625 °C for 15 minutes to simulate casting conditions

k) subsequently, mixing of the heat treated, broken test specimens of each sample as obtained in step j) with the respective mechanically reclaimed major part of each sample, obtained in step h) to obtain again a total amount of approximately 3 kg of broken material for each sample

l) repeating steps a) to k) in total 3 times to conduct 4 cycles in total.

[0088] For each cycle the numbering of the laboratory samples and the reference samples, prepared in step g), is increased by one. This means that in the second cycle the respective laboratory samples are designated "Laboratory sample A-II", "Laboratory sample B-II" and "Laboratory sample C-II" whereas the reference samples are designated "Reference sample Pozzolan II" and "Reference sample Clay II". This principle applies also to the third and fourth cycle. For example, the resultant laboratory samples and reference samples prepared in step g) of the fourth cycle are designated "Laboratory sample A-IV", "Laboratory sample B-IV" and "Laboratory sample C-IV", "Reference sample Pozzolan IV" and "Reference sample Clay IV", respectively.

[0089] The following parameters were measured throughout and/or after each cycle:

- Quantity and potassium content of the dust/fines (step f))

- Conductivity (DIN EN 27888) and pH (VDG Merkblatt P-26) of the dustless, particulate refractory compositions (step f))

- Analysis of the sand grain surfaces by means of an optical microscope

- Transverse strength levels (step i))

Determination of the quantity and potassium content of the dust:

[0090] After each cycle, the potassium content in the dust (K_2O_{Dust}) in [%] of each sample obtained in step f) was determined by X-Ray refraction analysis as potassium oxide. A potassium removal rate (PRR, determined in [% by weight]) was calculated for each cycle (4 cycles in total) and indicates the calculated *ratio* of a *dividend,* which is the

difference of the amount of potassium removed by removal of dust and the amount of potassium added by addition of the additive, to the *divisor,* which is the amount of potassium added by addition of binder, in the respective cycle.

[0091] The calculation was carried out according to the following formula:

$$PRR\ [\%] = [((K_2O_{Dust} * Dust) - (K2O_{ADD} * S_{cont.} * Add.Rate * 0{,}01)) / K_2O_{BIND}] * 100$$

wherein

K_2O_{Dust} means the potassium content in the dust in [%] determined by X-Ray refraction analysis,
Dust means the quantity of the dust in [%] of the total quantity of substrate before dedusting
K_2O_{ADD} means the content of potassium oxide in [%] of the solid additive before usage,
$S_{cont.}$ means the solid content of the additive suspension in [%],
$Add._{Rate}$ means the addition rate of the additive in [%] based on substrate and
K_2O_{BIND} means the amount of potassium hydroxide added by addition of binder in the respective cycle and was calculated as potassium oxide in [%].

[0092] In Figure 2 the calculated values are shown for the second, third and fourth cycle (x-axis), for each laboratory sample (labelled with A, B and C to refer to the "A"-, "B"- and "C"-series of the "Laboratory samples") and for the reference sample wherein the broken material was treated by means of the "Additive Pozzolan" (labelled with: Ref.).

[0093] The PRR values after the fourth cycle are shown in Table 3.

[0094] Table 3 and figure 2 show that aluminium hydroxide ("Laboratory sample A-IV") removes potassium ions from the broken material better than "Additive B", Additive C" and "Additive Pozzolan". Surprisingly, "Additive A" ("Laboratory sample A-IV") removes twice as much potassium ions than "Additive Pozzolan".

Table 3: Potassium removal rates (PRR) in [% by weight] after 4 cycles of "Laboratory sample A-IV", "Laboratory sample B-IV" and "Laboratory sample C-IV" (according to the invention) and "Reference sample Pozzolan IV" (not according to the invention):

	"Laboratory sample A-IV"	"Laboratory sample B-IV"	"Laboratory sample C-IV"	"Reference sample Pozzolan IV"
PRR [% by weight]	29,7	14,9	22,9	13,5

Conductivity, pH (VDG Merkblatt P-26) and acid demand (VDG Merkblatt P-26):

[0095] Conductivity, pH and acid demand were measured and determined for "Laboratory sample A-IV", "Laboratory sample B-IV", "Laboratory sample C-IV" as well as for "Reference sample Pozzolan IV". "Reference sample Clay IV" (broken material treated with the additive "Additive Clay") did not reach the cycle number 4. Thus, no conductivity, pH and acid demand could be determined for this reference sample during the fourth cycle. The results are summarized in Table 4.

Table 4: Conductivity, pH and acid demand after 4 cycles:

	"Laboratory sample A-IV"	"Laboratory sample B-IV"	"Laboratory sample C-IV"	"Reference sample Pozzolan IV"	"Reference sample Clay IV"
Conductivity [μS]	3780	1964	2530	3150	n./a.
pH	12,0	11,7	11,9	11,9	n./a.
Acid demand [mg HCl/100 g sand]	843	907	916	892	n./a.

Transverse strength levels:

[0096] The transverse strength levels after 1 and 4 hours (after 4 cycles) measured according to step i) for "Laboratory

sample A-IV", "Laboratory sample B-IV", "Laboratory sample C-IV" as well as for "Reference sample Pozzolan IV" are shown in Table 5. "Reference sample Clay IV" (broken material treated with the additive "Additive Clay") did not reach the cycle number 4. Thus, no transverse strength levels could be determined for this reference sample.

Table 5: Transverse strength levels in [N/cm^2] after 1 and 4 hours (after 4 cycles)

	"Laboratory sample A-IV"	"Laboratory sample B-IV"	"Laboratory sample C-IV"	"Reference sample Pozzolan IV"	"Reference sample Clay IV"
1h	113,3	31,7	71,7	106,7	n./a.
4h	181,3	66,3	131,3	180,0	n./a.

[0097] Note: Laboratory trials do not perfectly copy the conditions used in pilot plant trials or in practice. Results given above show trends, a direct comparison of data however might be misleading.

Analysis of the sand grain surfaces by means of an optical microscope.

[0098] Analysis of the sand grain surfaces was carried out by taking pictures of the sand grain surfaces after each cycle using an optical microscope (VHX550/1000D, Keyence). Significant differences were observed with increasing number of cycles. Broken material treated with aluminium hydroxide (A-series of "Laboratory samples") appeared very clean after each cycle. Broken material treated with a zeolite (B-series of "Laboratory samples") showed a slightly dusty surface. Broken material treated with a mixture of aluminium hydroxide and zeolite (C-series of "Laboratory samples") showed good results and appeared clean. However, broken material treated with the pozzolanic additive was slightly dusty whereas broken material treated with clay was very dusty, the degree of dustiness increased with the number of cycles. The results obtained after microscopic analysis after 4 cycles are summarized and evaluated in Table 6.

Table 6: Results after microscopic analysis of the sand grain surfaces (after 4 cycles)

	"Laboratory sample A-IV"	"Laboratory sample B-IV"	"Laboratory sample C-IV"	"Reference sample Pozzolan IV"	"Reference sample Clay IV"
Sand grain surface	very clean	dusty	clean	slightly dusty	very dusty
1=very good, 6=very bad	1	4	2-3	3	6

Example 3.2: CO_2-process (Carbophen process):

[0099] A test sample "Carbophen" was prepared on the basis of a CO_2-process as carried out by a person skilled in the art. The sample preparation was carried out as follows:

A) mixing of 2 kg new (virgin) silica sand (H31) with 40 g (2pbw) CO_2-Resol resin (Huettenes-Albertus (Carbophen 8178) for 120 seconds by means of a laboratory mixer

B) manufacturing six +GF+ transverse cores by shooting the mixture obtained in step A) in a core box and gassing said mixture in the core box with carbon dioxide for 15 seconds

C) measuring the transverse strength levels of the cores obtained in step B) (i) immediately (3 cores were measured) and (ii) after one hour (3 cores were measured)

D) collecting the used (measured) cores obtained in step C), and mechanical reclamation of said cores (preparation of broken material)

E) mixing for 60 seconds with the laboratory mixer the broken material obtained in step D) with 3 % by weight of "Additive C" (see "Example 1: Additive preparation and additive composition"), based on the total amount of broken material, resulting in a sample "Carbophen I", comprising broken material and approximately 1,3 % by weight of a

mixture of aluminium hydroxide and a zeolite (from "Additive C"), based on the total amount of broken material

F) subjecting sample "Carbophen I" obtained in step E) (i) to a heat treatment at 600 °C in a muffle furnace (Nabertherm L15/11) for 45 minutes and (ii) subsequently cooling the sample to a temperature below 40 °C to obtain a particulate refractory composition

G) homogenizing the particulate refractory composition obtained in step F) using the laboratory mixer for 30 seconds

H) dedusting, i.e. removing dust/fines from the particulate refractory composition obtained in step G) by screening said particulate refractory composition over a 125 μm sieve to obtain a dustless particulate refractory composition as well as a corresponding dust fraction

J) homogenizing the dustless particulate refractory composition obtained in step H) to obtain a homogenized, sieved and dustless particulate refractory composition

K) repeating steps A) to J), wherein in step A) the new (virgin) silica sand (H31) is replaced by the homogenized, dustless particulate refractory composition obtained in step J) of the first cycle

[0100] In the second cycle the resulting sample in step E) is "Carbophen II".

[0101] The homogenized, dustless particulate refractory composition obtained in step J) could be used to manufacture cores after both cycles. During the heat treatment of step F) no fritting/sintering was observed for the broken material mixed with "Additive C", in both cycles.

Example 3.3: CORDIS-process (inorganic binder):

[0102] Two test samples "CORDIS X", "CORDIS Y" and one reference sample "CORDIS Z" were prepared by the following steps:

A-I) separating broken material obtained from moulds and cores manufactured by the CORDIS®-process (the CORDIS-process was introduced by Hüttenes-Albertus Chemische Werke GmbH and is a process of manufacturing moulds and cores using an inorganic alkaline binder based on a solution comprising modified silicate, and additives) into three portions of equal amount, resulting in "Portion I", "Portion II" and "Portion III".

B-I) preparing/designated test samples:

- "Portion-I" was mixed with 3 % by weight of "Additive C" (see "Example 1: Additive preparation and additive composition"), based on the total amount of broken material, resulting in test sample "CORDIS X", comprising approximately 1,3 % by weight of a mixture of aluminium hydroxide and a zeolite (from "Additive C"), based on the total amount of broken material,
- "Portion II" was mixed with 6 % by weight of "Additive C" (see "Example 1: Additive preparation and additive composition"), based on the total amount of broken material, resulting in test sample "CORDIS X", comprising approximately 2,6 % by weight of a mixture of aluminium hydroxide and a zeolite (from "Additive C"), based on the total amount of broken material,
- "Portion III" was designated "CORDIS Z", no additive was added

C-I) subjecting each sample prepared/designated in step B-I) to a heat treatment at 600 °C in a muffle furnace (Nabertherm L15/11) for 45 minutes and subsequently cooling of each sample to obtain a particulate refractory composition of each sample

[0103] After step C-I) each particulate refractory composition of each sample was analyzed with respect to fritting/sintering. It was observed that severe fritting/sintering occurred in the reference sample "CORDIS Z". No fritting/sintering was observed in the test samples "CORDIS X" and "CORDIS Y", wherein the broken material was mixed with "Additive C" prior to heat treatment. Thus, no fritting/sintering is to be expected in the preparation of a particulate refractory composition for use in the manufacture of foundry moulds and cores, using "Additive C" to treat broken material obtained from the CORDIS-process.

Example 4: Quartz sand (SiO_2) fritting/sintering

[0104] Fine, powdery quartz sand (reactive SiO_2) was provided.

[0105] A first fraction of this sand was mixed with 10 % by weight of potassium hydroxide (KOH, solid), based on the total amount of fine, powdery quartz sand, resulting in test sample "Quartz I"

[0106] A second fraction of this sand was designated "Quartz II".

[0107] Subsequently, a test specimen from "Quartz I" and a test specimen from "Quartz II" were manufactured, suitable for analysis following the concepts of DIN 51730 (Testing of solid fuels - Determination of fusibility of fuel ash). The specimen had a cylindrical shape, a height of 3 mm and a diameter of 3 mm.

[0108] The test specimens obtained from the test samples "Quartz I" and "Quartz II" were subjected to a heat treatment (in the range of from 25 to 1650 °C) and were simultaneously analyzed following the concepts of DIN 51730 (Testing of solid fuels - Determination of fusibility of fuel ash). According to this analysis a cross sectional area (projection area) of a test specimen can be recorded in dependence of the temperature. During a heat treatment a test specimen shows various deformations and/or changes of the volume which leads to varying cross sectional area values (projection area values) in dependence of the temperature applied.

[0109] Heating from 25 °C to 700 °C was done with 80 °C/min, from 700 to 1500 °C with 50 °C/min and from 1500 °C with 10 °C/min.

[0110] The results of the analysis following the concepts of DIN 51730 are shown in Figure 1. The two curves in Figure 1 show the correlation of the cross sectional area values (projection area values; in rel. %, where 100 % refer to the starting area values of each test specimen prior to heating) of test specimens from "Quartz I" and "Quartz II" and the temperature applied. The curves are labeled as follows: A refers to "Quartz I" and B refers to "Quartz II". The cross sectional area values (projection area) indicate the progress of fritting/sintering. Fritting/sintering can be observed by a decreasing projection area (due to volume contraction), where the area decrease is not accompanied by a change of the shape of the test specimen. Thus, decreasing values indicate fritting/sintering. Figure 1 shows that in the presence of 10 % potassium hydroxide (KOH, solid) fine quartz sand (SiO_2) exhibits a clear tendency to form agglomerates (fritting/sintering products) (see "Quartz I" in Fig. 1). Fritting/sintering started at a temperature of approximately 475 °C and was intensified upon increased temperatures. In contrast, "Quartz II" did not show any signs of fritting/sintering. Thus, the combination of fine, powdery SiO_2 (reactive SiO_2) and KOH should be avoided during the heat treatment of broken material, because fritting/sintering under this conditions is already observed at temperatures significantly below the temperatures typically applied in practice for a heat treatment (i.e., temperatures in the range of 580-600 °C).

Claims

1. Method of preparing a particulate refractory composition for use in the manufacture of foundry moulds and cores from spent foundry moulds or cores formed of refractory material and an alkaline binder containing alkali metal ions, the method comprising the following steps:

   - providing broken material from spent foundry moulds or cores or preparing broken material from spent foundry moulds or cores,
   - mixing the broken material with an additive comprising or consisting of one or more particulate constituents selected from the group consisting of aluminium hydroxide, synthetic zeolites and natural zeolites
   and
   - subjecting the mixture to a heat treatment at a temperature in the range of from 400 to 750 °C.

2. Method according to claim 1, wherein the alkaline binder containing alkali metal ions is an organic phenol/formaldehyde resin binder.

3. Method according to claim 1, wherein the alkaline binder containing alkali metal ions is an inorganic binder.

4. Method according to any preceding claim, wherein the amount of constituents in the additive is selected such that sintering and/or fritting is reduced during the heat treatment in comparison with a method not comprising mixing the broken material with an additive but being otherwise identical.

5. Method according to any preceding claim, wherein the heat treatment is at a temperature in the range of from 400 to 750 °C, more preferably 450 to 670 °C, even more preferably 530 to 650 °C, most preferably 580 to 600 °C.

6. Method according to any preceding claim, wherein the binder is an alkaline phenol/formaldehyde resin binder (Resol),

preferably as used in a method of bonding foundry sand with phenolic resin binder in alkaline aqueous solution, wherein the binder is cured with an liquid or gaseous organic ester or with gaseous carbon dioxide.

7. Method according to any preceding claim, wherein the additive comprises said constituents suspended in water.

8. Method according to any preceding claim, wherein simultaneously with being subjected to said heat treatment the mixture is fluidized in a fluidized bed apparatus or moved in a thermal sand reclamation unit.

9. Method according to any preceding claim, wherein solid matter containing alkali metal ions is removed from the mixture during and/or after the heat treatment, so that the concentration of alkali metal ions in the remaining mixture decreases,.
wherein said solid matter preferably comprises particulate constituents of said additive and/or reaction products thereof.

10. Method according to any preceding claim, wherein the additive comprises one or more particulate constituents selected from the group consisting of
amorphous aluminium hydroxide ($Al(OH)_3$) monoclinic aluminium hydroxide ($Al(OH)_3$), and hexagonal aluminium hydroxide ($Al(OH)_3$),
synthetic zeolites selected from the group consisting of synthetic mordenite, zeolite A, zeolite L, zeolite X, zeolite Y, ZM5 and ZSM11, and (other) zeolites of the pentasil family of zeolites,
natural zeolites selected from the group consisting of analcime, barrerite, chabazite, brewsterite, clinoptilolite, edingtonite, erionite, ferrierite, gismondine, gmelinite, gonnardite, harmotome, heulandite, laumontite, levynite, mesolite, mordenite, natrolite, paulingite, pentasil, phillipsite, pollucite, scolecite, stellerite, stilbite and wairakite.

11. Method according to any preceding claim, wherein at least a part of the particulate constituents of the additive passes a screen (according to DIN ISO 3310) having a mesh size of 125μm.12. Method according to any preceding claim, wherein the total amount of aluminium hydroxide, synthetic zeolites and natural zeolites in the mixture is in the range of from 0.1 to 3 % by weight based on the total weight of broken material, aluminium hydroxide, synthetic zeolites and natural zeolites.

12. Particulate refractory composition for use in the manufacture of foundry moulds and cores, obtainable by a method according to any preceding claim.

13. Method of making a foundry mould or core comprising the following steps:

- preparing a particulate refractory composition according to any of claims 1 to 12, or providing a particulate refractory composition for use in the manufacture of foundry moulds and cores according to claim 13,
- mixing the particulate refractory composition with a binder
- shaping the resulting mixture, and
- curing the binder in said shaped mixture.

14. Method of making a foundry mould or core according to claim 14, wherein the binder is cured with a liquid or gaseous organic ester or with gaseous carbon dioxide.

15. Use of a suspension comprising one or more particulate constituents selected from the group consisting of aluminium hydroxide, synthetic zeolites and natural zeolites

(i) for reducing the likelihood of sintering and/or fritting during heat treatment at a temperature in the range of from 400 to 750 °C of broken material from spent foundry moulds or cores
and/or
(ii) for removing alkali metal ions from broken material from spent foundry moulds or cores.

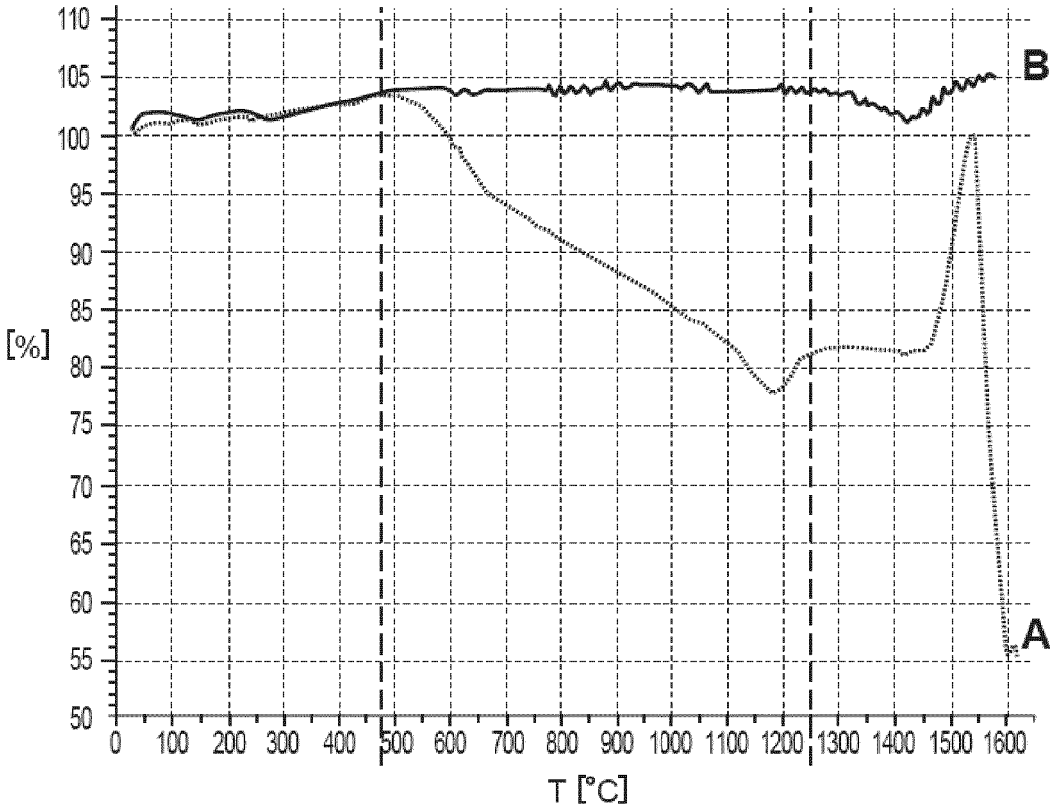
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Fig. 1

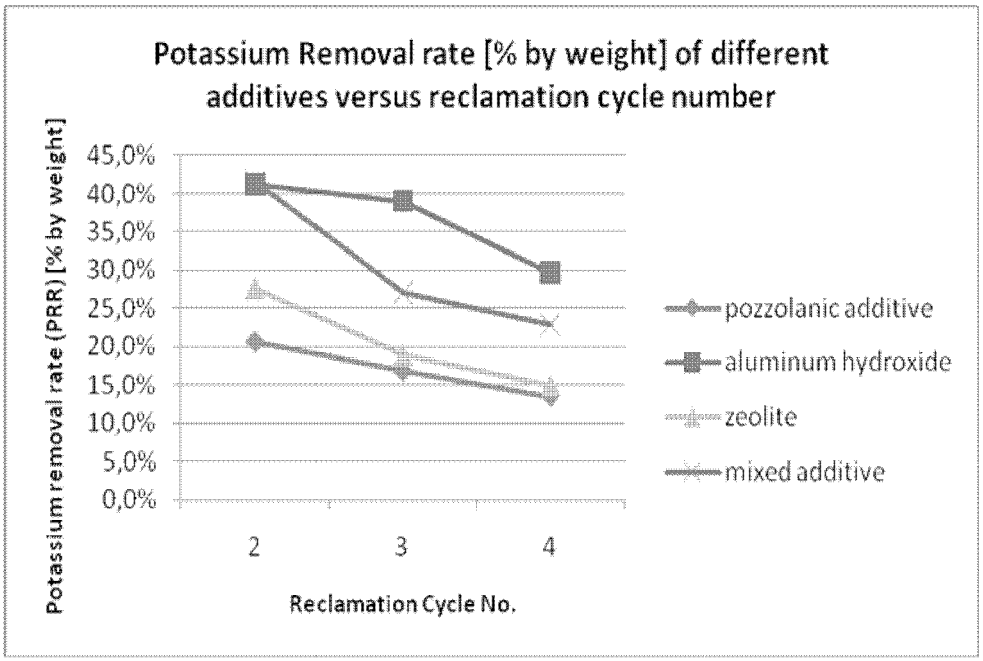
Potassium Removal rate [% by weight] of different additives versus reclamation cycle number
Potassium removal rate (PRR) [% by weight]
45,0%
40,0%
35,0%
30,0%
25,0%
20,0%
15,0%
10,0%
5,0%
0,0%
2
3
4
Reclamation Cycle No.
pozzolanic additive
aluminum hydroxide
zeolite
mixed additive

Fig. 2

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EUROPEAN SEARCH REPORT

Application Number
EP 12 17 8533

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X : particularly relevant if taken alone
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