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(54) Method and composition for the preparation of foundry moulds and cores

(57) A foundry moulding composition, a method for making the foundry moulding composition and a method for the manufacture of foundry moulds and cores using the foundry moulding composition.

The foundry moulding composition comprises sand, a binder and silica fume and/or a silica fume substitute, wherein the sand comprises reclaimed sand comprising alkaline binder residues. In one embodiment the alkaline binder residues comprise one or more of potassium silicate, sodium silicate, potassium carbonate (potash), sodium carbonate (soda), sodium hydroxide, potassium hydroxide, sodium acetate and potassium acetate.

The reclaimed sand comprises alkaline binder residues as a result of being bonded by an inorganic or mixed organic-inorganic binder. The alkaline (inorganic) residues do not burn out during casting and usually lead to low reclamation rates. The use of silica fume is considered to improve the properties of reclaimed sand comprising alkaline binder residues.

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Description

[0001] The invention relates to a method and composition for the preparation of foundry moulds and cores from reclaimed sand. More particularly, the invention relates to methods for improving the strength of moulds made from alkaline phenolic reclaimed sand, using a composition comprising silica fume and/or a silica fume substitute.

[0002] Due to the restrictions imposed on the disposal of used resin-coated sand from spent foundry moulds, together with the high cost of new sand, the reclamation of foundry moulding sand is a matter of increasing importance.

[0003] Sand may be reclaimed from spent moulds using a number of techniques. Wet reclamation involves crushing the sand to grain size and washing off residues with water, followed by drying the sand. The process results in sand having a high re-bonding strength, but due to the high energy cost of drying the sand and the expensive water treatment required to permit safe disposal of the wash water, its use is not common.

[0004] Thermal reclamation involves heating the sand to a sufficiently high temperature to burn or decompose any remaining binder residues. Thermal reclamation is costly due to the large energy requirements and expensive equipment.

[0005] The most commonly used technique, mechanical reclamation, comprises attrition and grinding to break up the sand into individual particles and remove binder residues, although not all binder residues can be removed using this process. Depending on the binder system used, it is possible to satisfactorily re-bond mechanically reclaimed sand for moulding at high levels of 90% and above (even up to 100%). For example, a number of organic binder systems such as acid-cured furan resins do not experience any significant loss in performance with reclaimed sand. Many foundries regularly use reclaimed sand at addition levels of 80 to 90%, with the addition of 10 to 20% clean (new) sand for consistency and for practical reasons e.g. making up for handling losses of sand during the foundry processes. In contrast, inorganic binder systems such as those based on sodium silicate and so-called mixed organic-inorganic binders such as ester-cured alkaline phenolic resins, are difficult to reclaim at high percentages because no burn-out of the inorganic material occurs. The build up of alkali (alkaline) residues such as potassium and/or sodium silicate, potash and/or soda, in the reclaimed sand can lead to a reduction in the working time of the sand (mixed sand bench life), the rate of strength development, the final cured strength and the mould quality (surface finish and hardness). Attrition reclamation of alkaline phenolic bonded sand is therefore limited to a practical level of about 70%, although re-use levels of 80% and higher may be possible in some foundries due to their different process parameters and moulding requirements.

[0006] It is therefore desirable to improve the bonding properties of sand obtained by reclamation of used sand, particularly used sand containing inorganic binder residues. For example, the properties may be improved such that an increased proportion of reclaimed sand and/or a reduced amount of binder are used in the manufacture of new moulds or cores.

[0007] US 6,015,846 describes a composition for improving the properties of sand reclaimed thermally comprising a particulate clay additive.

[0008] US 5,190,993 describes a method for improving the tensile strength of reclaimed sand bonded with an ester cured alkaline phenolic resin comprising treating the sand with a solution of an aminosilane.

[0009] EP 1 753 560 describes a method of thermal reclamation in which the sand is treated with a particulate pozzolan additive prior to heating at a temperature of between 450 and 900°C. The patent teaches the removal of dust and/or fines during and/or after the heat treatment to remove both sand fines and the pozzolanic additive. This step is said to be desirable due to the negative effect of residual pozzolanic additive on the re-bond strength of the sand.

[0010] According to a first aspect of the present invention there is provided a foundry moulding composition for the manufacture of foundry moulds and cores comprising sand;
a binder; and
silica fume and/or a silica fume substitute,
wherein the sand comprises reclaimed sand comprising alkaline binder residues.

[0011] It will be understood that the reclaimed sand will comprise alkaline binder residues as a result of being bonded by an alkaline inorganic or mixed organic-inorganic binder. In some embodiments, the alkaline residues will be one or more of potassium silicate, sodium silicate, potassium carbonate (potash), sodium carbonate (soda), sodium hydroxide, potassium hydroxide, sodium acetate and potassium acetate. This type of sand suffers from low reclamation rates because the alkaline (inorganic) residues do not burn out during casting and are difficult to mechanically remove (via attrition) from the sand during reclamation. Certain residues such as potassium silicate may also be formed by the action of inorganic hydroxides in the binder reacting with the silica sand at the elevated casting temperatures. These alkaline residues have a deleterious effect on the strength properties of re-bonded used sand. It has surprisingly now been found that the use of silica fume as a sand additive improves the re-bonding properties of reclaimed sand. The inventors believe that the acidic nature of the silica fume may provide a benefit in relation to the alkaline residues.

[0012] Silica fume is a very fine amorphous silica. It is produced in electric arc furnaces as a by-product during the production of elemental silicon or silicon-containing alloys such as ferrosilicon. Silica fume has a high silicon dioxide content (usually at least 85%), an extremely small particle size and large surface area. The physical properties of silica fume are typically: bulk density = 120 to 450kg/m^3 (as-produced), bulk density = 450 to 750kg/m^3 (densified), specific gravity = 2.1 to 2.4 and surface area (BET) = 13 to 30m^2/g.

[0013] Silica fume is a highly reactive pozzolan used extensively as an admixture for concrete and cementitous products. A pozzolan is a siliceous or siliceous and aluminous material which in itself possesses little or no cementitious value but will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide to form compounds possessing cemetitious properties (pozzolanic activity). ASTM C 1240 provides the standard specification for silica fume used in cementitious mixtures.

[0014] Silica fume is also commonly referred to as condensed silica fume, microsilica or silica dust. Silica fume is distinct from, and does not include within its scope, the materials precipitated silica, fumed silica, gel silica, colloidal silica or silica flour.

[0015] Precipitated silica typically has a surface area (BET) of 150-250m^2/g (much greater than silica fume), a tamped i.e. densified density of ca 80-250kg/m^3 and a specific gravity of ca 2.0. It should be noted that some granulated forms are available, with higher bulk densities etc.

[0016] Fumed silica typically has a surface Area (BET) of 35-65m^2/g (greater than silica fume), a specific surface area of 175-225m^2/g, an undensified density of 40-60kg/m^3; a densified density of 120-140kg/m^3 and an average primary particle size of 40nm (0.04μm). It should be noted that some granulated forms are available, with higher bulk densities etc. Fumed silica is not a suitable additive for sand. Its very small particle size and associated large volume/weight and surface area/weight would give a sand mixture which had poor flowability ('heavy') and be difficult to compact. Furthermore, a very high level of binder would be required in order to coat all of the particles (high binder demand) and maintain the necessary mould or core strength.

[0017] Silica gel is a hygroscopic material produced in a very large range of particle sizes up to mm in diameter.

[0018] Colloidal silica is typically a solution containing 25-30% SiO_2 having a particle size 20-40nm (0.02 - 0.04microns).

[0019] Silica Flour is a crystalline silica (silica fume comprises amorphous silica) usually produced by ball-milling silica sand.

[0020] It will be understood that a silica fume substitute is a material which comprises silica and has a pozzolanic activity similar to silica fume. The silica fume substitute has the same or similar physical and/or chemical properties as silica fume and can be used instead of some or all of the silica fume in the composition. Silica fume substitute does not include within its scope the materials precipitated silica, fumed silica, gel silica, colloidal silica, silica flour, fly ash (typical SiO_2 content = 35-48%, typical surface area = 400-700m^2/kg) or calcined bauxite.

[0021] In one embodiment, the silica fume substitute is Rice Husk Ash (RHA). RHA is a reactive pozzolan generated when risk husks are burnt, and known as a replacement for silica fume in high strength concrete and other applications. RHA comprises typically 80-90% amorphous silica.

[0022] In some embodiments, the composition comprises silica fume and/or a silica fume substitute in an amount of at least 0.05%, at least 0.1%, at least 0.15%, at least 0.2%, at least 0.25%, at least 0.3%, at least 0.4% or at least 0.5% by weight of sand.

[0023] In certain embodiments, the composition comprises silica fume and/or a silica fume substitute in an amount of no more than 5%, no more than 4%, no more than 3%, no more than 2.0%, no more than 1.5%, no more than 1.0% or no more than 0.5% by weight of sand.

[0024] Silica fume may form from 0 to 100wt% of the total amount of silica fume and silica fume substitute. In one embodiment, silica fume forms at least 50wt%, at least 60wt%, at least 70wt%, at least 80wt% at least 90wt% or 100wt% of the total amount of silica fume and silica fume substitute.

[0025] Silica fume has a typical particle size range of 0.1 to 1.0μm (average value being between 0.10 and 0.15μm), however particle size analysis often shows the presence of a large amount of agglomerated particles having average sizes between 10 and 100μm. Some agglomerates are difficult to break due to strong bonds being produced during silicon smelting, hence the results of conventional size measurements are often significantly different from the true particle size distribution. Modern laser particle size analysers with built-in ultrasound, used with special dispersants have been used to accurately measure the particle sizes quoted above.

[0026] A d90 value is a convenient measure for quoting particle sizes. The term d90 means that 90% of the particles have a size below and up to a value 'X'. In one series of embodiments, the particle size (d90) of the silica fume and/or silica fume substitute (when measured using a laser particle size analyser) is no more than 100μm, no more than 50μm, no more than 40μm, no more than 30μm, no more than 20μm, no more than 10μm, no more than 5μm, no more than 2 μm, no more than 1μm or no more than 0.5μm.

[0027] In one series of embodiments, the SiO_2 content of the silica fume and/or the silica fume substitute is at least 75wt%, at least 80wt%, at least 85wt%, at least 90wt% or at least 95wt%. In another series of embodiments, the SiO_2 content of the silica fume and/or the silica fume substitute is no more than 99wt%, no more than 97wt%, no more than 95wt% or no more than 90wt%.

[0028] It will be understood that sand will constitute the majority of the foundry moulding composition. In an embodiment, the composition comprises at least 90wt%, at least 95wt% or at least 97wt% sand.

[0029] The composition may comprise fresh sand in addition to the reclaimed sand. Conveniently, at least 50wt% of the sand present in the composition will be reclaimed sand since it is commercially and environmentally advantageous to recycle used sand rather than purchase new sand and dispose of used sand. In one series of embodiments, at least 50wt%, at least 55wt%, at least 60wt%, at least 65wt%, at least 70wt%, at least 75wt%, at least 80wt%, at least 85wt% or at least 90wt% of the sand in the composition is reclaimed sand. In other embodiments, no more than 95wt%, no more than 90wt%, no more than 85wt%, no more than 80wt% or no more than 75wt% of the sand is reclaimed sand. In a particular embodiment, 100% of the sand is reclaimed sand.

[0030] By 'reclaimed sand', it will be understood that the sand is reclaimed from spent foundry moulds or cores and is therefore contaminated by, inter alia, binder residues. Spent foundry moulds or cores are the moulds or cores that are remaining after metal casting and removal of the cast metal shapes.

[0031] By 'fresh sand' or 'new sand', it will be understood that the sand has not been reclaimed from a spent foundry mould or core and so does not comprise binder residues.

[0032] The reclaimed sand may be reclaimed by mechanical reclamation, thermal reclamation, wet reclamation, or by any other method of reclamation. In one embodiment, the sand is reclaimed by mechanical reclamation. In a further embodiment, the reclaimed sand has not been subject to thermal reclamation. Such an embodiment is advantageous because thermal reclamation is an expensive process.

[0033] The alkaline residues may be residues from an alkaline inorganic or a mixed organic-inorganic binder. The inorganic or mixed organic-inorganic binder may be a self-hardening (also known as self-set, no bake or cold-setting) binder such as an ester-cured binder. Alternatively the inorganic or mixed organic binder may be a gaseous or heat triggered binder, such as a CO_2 gas-cured binder or a binder cured by a volatile ester such as methyl formate.

[0034] In one embodiment, the inorganic binder is a sodium/potassium silicate binder and the mixed organic-inorganic binder is an alkaline phenolic binder.

[0035] In one embodiment, the reclaimed sand is ester-cured or CO_2- cured alkaline phenolic bonded sand. In another embodiment, the reclaimed sand is an ester-cured or CO_2-cured sodium silicate bonded sand.

[0036] In one embodiment the reclaimed sand has a pH of at least 8, at least 9, at least 10 or at least 11. In a further series of embodiments, the reclaimed sand has a pH of less than 12, less than 11, or less than 10.

[0037] In one series of embodiments the reclaimed sand has an alkalinity of at least 0.5%, 1%, 1.5%, 2%, 2.5%, 3%, 4%, 5%, 6%, 7%, 8%, 9% or 10%. In another series of embodiments, the reclaimed sand has an alkalinity of no more than 10%, 9%, 8%, 7%, 6%, 5%, 4%, 3% or 2%.

[0038] Alkalinity is determined by an acid-base titration. Alkalinity may be measured using the Acid Demand Test. An amount of sand (W_1 e.g. 50g) is mixed with 50ml 1 N hydrochloric acid (HCl) and left to stand (e.g. for 24 hours). The mixture is then titrated to neutral (pH 7) using 1 N sodium hydroxide (NaOH). The titre value (T_1) is subtracted from the 50ml HCl to give the Acid Demand Value. The alkalinity is calculated by dividing the Acid Demand Value by the weight of sand as follows:

$$\text{Alkalinity} = (50 - T_1) \times 100/W_1$$

[0039] The foundry moulding composition comprises a binder so that the sand can be bonded to form a foundry mould or core. The binder may be any binder suitable for making sand moulds and cores and is not limited to inorganic and mixed organic-inorganic binders. In some cases the foundry will reclaim its sand on site, in which case it may be convenient to employ the same binder that was used to bond the sand for previous castings. The binder may be cured by contact with a chemical hardener in a self-hardening system. Alternatively, the binder may be cured by triggered hardening, for example by the application of heat or a reactive gas or a vaporised liquid hardener.

[0040] In some embodiments, the binder is present in the composition in an amount from 0.1 to 5%, from 0.5 to 3%, from 1 to 2%, or from 1.2 to 1.8% by weight of sand.

[0041] Alkaline binders suitable for use with a chemical hardener include organic resins such as an alkaline phenolic resole resin or inorganic binders such as sodium or potassium silicates. The composition may further comprise a chemical hardener. Suitable chemical hardeners include liquid organic esters. In certain embodiments, the chemical hardener is present in the composition in an amount of 8 to 35%, 10 to 30%, or 12 to 25% by weight of binder.

[0042] In one embodiment, the binder is an alkaline phenolic resin. Alkaline phenolic resin can be cured by its reaction with an ester. In one embodiment, the ester is a liquid organic ester or a blend of liquid organic esters. FENOTEC® resins are a range of commercially available alkaline phenolic resole resins and FENOTEC® hardeners are a range of commercially available liquid organic ester hardener blends.

[0043] The composition may additionally comprise water.

[0044] In certain embodiments, the composition comprises water in an amount of at least 0.05%, at least 0.1%, at least 0.15%, or at least 0.2% by weight of sand.

[0045] In certain embodiments, the composition comprises water in an amount of no more than 2.0%, no more than 1.5%, no more than 1.0% or no more than 0.5% by weight of sand.

[0046] In certain embodiments, the composition comprises further minor components, such as silane, surfactants, suspension agents, dispersion agents and stabilisers, biocide and/or anti-foaming agents.

[0047] Suitable suspension or dispersion agents include organic polymers (salts of polymeric acids) and modified clays (based on bentonite or attapulgite). Suitable attapulgite based products are available commercially from BASF Corporation (based in Germany), supplied under the Attagel® range of thickeners and rheology modifiers. In certain embodiments, the composition further comprises one or more suspension agents in an amount of at least 0.0001%, at least 0.001%, at least 0.01% or at least 0.1 % by weight of sand but no more than 1%, no more than 0.5%, no more than 0.2%, no more than 0.1%, no more than 0.07%, no more than 0.04% or no more than 0.02% by weight of sand.

[0048] In certain embodiments, the composition further comprises silane in an amount of at least 0.001% by weight of sand but no more than 0.2%, no more than 0.1%, no more than 0.05% or no more than 0.03% by weight of sand.

[0049] According to a second aspect of the invention there is provided a method for preparing a foundry moulding composition, comprising mixing sand, a binder and silica fume and/or a silica fume substitute,
wherein the sand comprises reclaimed sand comprising alkaline binder residues.

[0050] Typically the sand, the binder and the silica fume and/or a silica fume substitute will be mixed in a conventional continuous mixer to form the composition.

[0051] The silica fume and/or a silica fume substitute may be employed as a dry solid or, more conveniently, as a suspension in a liquid carrier, e.g. as a slurry. The liquid carrier may be water. In an embodiment, the slurry has a solids content of from 20 to 75%, from 30 to 70% or from 40 to 60%. In a particular embodiment, the slurry has a solids content of 50%.

[0052] In an embodiment where the silica fume and/or a silica fume substitute is employed in a slurry, the slurry may be mixed with the binder and the sand in an amount of from 0.05% to 3%, from 0.1 % to 2%, from 0.2% to 1%, or from 0.3 to 0.8% by weight of sand. The slurry may comprise further components in addition to silica fume/silica fume substitute and a carrier material. In one embodiment, the slurry comprises one or more of silane, surfactants, rheology modifiers, dispersion agents, anti-foaming agents, biocide and/or suspension agents.

[0053] In one embodiment, the method further comprises reclaiming sand that is bonded by an alkaline inorganic or a mixed organic-inorganic binder and subsequently mixing at least some of the reclaimed sand with the binder, the silica fume and/or a silica fume substitute, and optionally fresh sand to prepare the foundry moulding composition. In such an embodiment, the sand reclamation process may comprise breaking up spent foundry moulds and cores to obtain sand for preparation of the foundry moulding composition. The sand may be reclaimed using mechanical, thermal or wet reclamation to reclaim the sand. The method of reclamation may additionally comprise the removal of dust and fines from the reclaimed sand prior to the preparation of the foundry moulding composition. In a particular embodiment, the sand is not reclaimed by thermal reclamation. In a particular embodiment, the sand is not reclaimed by wet reclamation.

[0054] In one embodiment of the second aspect of the invention, the method for preparing the foundry moulding composition comprises an additional initial step of reclaiming sand that is bonded by alkaline inorganic or mixed organic-inorganic binder and subsequently mixing the reclaimed sand with a binder, silica fume and/or a silica fume substitute and optionally fresh sand.

[0055] According to a third aspect of the invention there is provided a method for making a foundry mould or core comprising
preparing a foundry moulding composition comprising sand, a binder, silica fume and/or a silica fume substitute, and optionally a chemical hardener;
forming the composition into a desired pattern or shape; and curing the binder,
wherein the sand comprises reclaimed sand comprising alkaline binder residues.

[0056] The binder may be cured by contact with a chemical hardener in a self-hardening system. Alternatively, the binder may be cured by triggered hardening, for example by the application of heat or a catalyst gas or a vaporised hardener. It will be understood that the foundry moulding composition must comprise a chemical hardener if the binder is to be cured without the use of a thermal or gaseous trigger.

[0057] In one embodiment, the binder is an alkaline phenolic resin.

[0058] In one embodiment the chemical hardener is an organic ester.

[0059] The conditions under which the curing takes place will depend on the characteristics of the binder employed and are well known.

[0060] The method for preparing the foundry mould or core may comprise first preparing a foundry moulding composition by reclaiming sand that is bonded by an alkaline inorganic or a mixed organic-inorganic binder and mixing the reclaimed sand with a binder, silica fume and/or a silica fume substitute and optionally fresh sand.

[0061] The invention will now be described by way of example only.

Methodology

[0062] Test cores were produced from a mixture of reclaimed and new sand obtained from three foundries mechanically reclaiming alkaline phenolic ester bonded sand. All foundries were using Foseco Pty Australia's FENOTEC® resin and hardener. Foundry A was reclaiming at reclamation level of 70%, Foundry B and C were reclaiming at a level of 80%. Test cores were also produced from a mixture of reclaimed and new sand obtained from a fourth foundry D, which was reclaiming at a level of 50%, sand that had been bonded with a sodium silicate binder (2.35 ratio SiO_2:Na_2O) and ester hardener (propylene carbonate / triacetin blend). The reclaimed sand had the properties as shown in table 1:

Table 1

	Reclaimed Sand A	**Reclaimed Sand B**	**Reclaimed Sand C**	**Reclaimed Sand D**
AFS[1] Grain Fineness No	49.99	46.54	38.48	39.2
Moisture Content	0.1%	0.37%	0.23%	0.16%
Loss On Ignition @1000°C	0.23%	1.00%	1.16%	0.25%
Alkalinity:	0.92%	1.42%	2.9%	3.72%
pH	10.15	n/k	10.38	10.3
[1]American Foundry Society				

[0063] The ester set resins used for testing were low viscosity alkaline phenolic resins supplied by Foseco Pty - FENOTEC® 888, a potassium hydroxide based resin, and FENOTEC® 810, a mixed sodium/potassium hydroxide based resin. The hardener used was FENOTEC® H20, a triacetin-based liquid organic ester blend supplied by Foseco Pty. The carbon dioxide gas cured resin was an alkaline phenolic resin supplied by Foseco Pty under the trade name ECOLOTEC® 750.

[0064] Two grades of commercially available of silica fume were used, having the following properties:

Table 2 - Properties of Silica Fume

	SF X	**SF Y**
SiO_2 content	min 88.0% (93.0% typical)	min 98.0% (98.4% typical)
Moisture	0.5% (typical)	0.5% max (0.2% typical)
Loss On Ignition (LOI) @975°C	1.0% (typical)	0.8% max (0.5% typical)
pH (typical)	2.0-3.5	5.5-7.5 (6.8 typical)
Particle size	<0.8 μm (90%)	<45 μm
Coarse Particles (>45μm (325 mesh))	1.0% max (0.3% typical)	0.5% max (0.2% typical)
Surface Area	15 m^2/g (typical)	n/k
Undensified Bulk Density (when packed) (as produced)	200-300 kg/cm^2	250-350 kg/cm^2 (300 typical)
Densified Bulk Density (when packed)	n/k	450-550 kg/cm^2 (500 typical)

[0065] The standard laboratory test method for studying ester hardened resin binders, was to take a sand mixture sand comprising 70-85% by weight reclaimed sand (ex Foundry A, B or C) and 30-15% new sand. To this mixture was added FENOTEC® 888 resin in an amount of 1.6% by weight of sand, and FENOTEC® H20 hardener in an amount of 23% by weight of resin. This mixture was tested without further additions (control 1), with the addition of water in an amount as stated (controls 2 and 3), with the addition of solid material (including silica fume) and a separate water addition, or with the addition of a slurry having a solids content as stated (typically 50wt%).

[0066] The sand (2kg) was placed in Kenwood Kitchen mixer and any required additions (water, solid material or slurry) added to the sand and mixed for two minutes. 7.36g of FENOTEC® H20 hardener was then added and mixed for approximately one minute, followed by an addition of 32g of FENOTEC® resin and mixing for a further 1 minute. Immediately after mixing, the sand was used to form standard AFS tensile sand cores ("dog-bones") using a Ridsdale Dietert core box. The cores were stored at room temperature (typically 20-22°C and a relative humidity of 40-65%) and their strength was measured at intervals of 30 minutes, 1 hour, 4 hours and 24 hours. Tensile strengths (in psi) were measured on a Monsanto Tensometer fitted with a Tensile Core Strength Accessory.

[0067] After mixing of the binder and the hardener with the sand, the mixed sand has a limited time during which the mould or core must be formed. This is known as the bench life or work time, after which the mixture stops being free flowing and begins to become heavy and difficult to compact, and any sand cores or mould produced after this time will have poor strengths and be friable. The bench life was measured as the time from the start of mixing to the time at which a core reached a hardness of 50 as measured using a Green Hardness "B" Scale Tester as supplied by Dietert Co, Detroit, Michigan USA. This instrument accurately measures surface hardness of sand moulds and cores by pressing the tester against the mould surface and noting the reading on the dial. The tester uses a spring loaded ball, and a mould offering no resistance would have a zero reading, one having a hardness capable of preventing any penetration would read 100.

[0068] The strip time is the time taken for the mould or core to reach handleable strength i.e. the time after mixing when most moulds and cores can be stripped from the pattern without damage or risk of distortion. For ester-hardened alkaline phenolic resins and ester-hardened silicate binders, the ratio of strip time (ST) to bench life (BL) is extended when using reclaimed sand, as compared to when using new sand. The degree of extension depends on the type of reclaimed sand and the residues present. The increased ratio reduces the overall productivity of the moulding process because it takes longer for the mould to be stripped before another can be produced from the moulding pattern. The strip time was measured as the time from the start of mixing at which the moulds reaches a hardness of 85 on a Dietert Green Hardness "B" Scale Tester.

[0069] The standard laboratory test method for studying carbon dioxide gas cured resin binders, was to take a sand mixture comprising a mixture of 50% by weight reclaimed sand (Foundry A or D) and 50% new sand. To this mixture was added ECOLOTEC® 750 resin in an amount of 2.0% by weight of sand. This mixture was tested without further additions (control 1), or with a slurry having a solids content as stated (typically 55wt%).

[0070] The sand (2kg) was placed in Kenwood Kitchen mixer and any required additions (water, solid material or slurry) added to the sand and mixed for two minutes. 40g of ECOLOTEC® 750 resin was then added and the sand mixed for a further 1 minute. Immediately after mixing, the sand was used to form standard AFS tensile sand cores ("dog-bones") using a Ridsdale Dietert core box. The cores were cured ("gassed") by passing carbon dioxide through the core for 30 seconds at a flow rate of 12 litres per minute and gas temperature of 25-28°C. The cores were stored at room temperature (typically 20°C and a relative humidity of 55-65%) and their strength was measured at intervals of 5 minutes, 1 hour, 24 hours and 7 days. Tensile strengths (in psi) were measured on a Monsanto Tensometer fitted with a Tensile Core Strength Accessory.

Example 1 - Addition of silica fume

[0071] The effect of adding solid silica fume (SF X) to a mixture of 80% reclaimed sand B and 20% new sand bonded with FENOTEC® 888 resin and FENOTEC® H20 hardener was studied as detailed below in table 3.

Table 3

	Control 3	**Example 1a**	**Example 1b**
Water Addition (BOS)	0.3%	0.3%	0.6%
Silica Fume (BOS)	-	0.2%	0.8%
Tensile Strength[1]			
½ hour	11	14	16
1 hour	24	28	29
4 hour	39	45	45
24 Hr	65	67	72

(continued)

	Control 3	Example 1a	Example 1b
Bench Life (min)	7	7	7
Strip Time (min)	14	11½	11
[1] Ambient temperature 20°C; relative humidity 45-50%; sand temperature 18°C.			

[0072] As shown in Table 3, the tensile strengths of the cores made with silica fume (Examples 1 a and 1 b) and a water addition were higher than the tensile strength of the control made with an addition of water only. In addition, there was a notable decrease in the mixed sand strip time, with no change in bench life.

Example 2 - Comparison of different pozzolanic additives

[0073] The effect of adding a slurry (50% dry solids) of silica fume (SF X) or other pozzolanic additives to a mixture of 70% reclaimed sand A and 30% new sand bonded with FENOTEC® 888 and FENOTEC® H20 hardener was studied as detailed below in table 4.

Table 4

	Control 1	Control 2	Comparative Example 2a	Comparative Example 2b	Example 2
Pozzolanic additive slurry 0.5% BOS	-	-	Fly Ash	Calcined Bauxite	Silica Fume
Water Addition	-	0.25%	-	-	-
Tensile Strength[1]					
½ hour	20	19	18	19	23
1 hour	28	27	28	25	29
4 hour	51	52	45	40	56
24 Hr	59	60	59	55	64
Bench Life (min)	6½	6½	6	6	6
Strip Time (min)	11	11	10	9½	9½
[1]Ambient temperature 21°C; relative humidity 45-65%; sand temperature 19°C.					

[0074] As shown in Table 4, the tensile strengths of the cores made with silica fume slurry (Example 2) were consistently higher than the tensile strength of the cores made with no additive or with other pozzolanic additives, at every time point tested during curing.

Example 3 - silica fume slurries with further additives

[0075] Six different slurry formulations of silica fume were prepared by adding the solid components (silica fume (SF X) and Attagel® 50) to water, optionally followed by silane and surfactant, according to table 5a:

Table 5a

	Ex 3a	Ex 3b	Ex 3c	Ex 3d	Ex 3e	Ex 3f
Water (%)	49.5	49.7	47.5	48.5	48	50
Attagel® 50[1]	0.5	0.3	0.5	0.5	0.5	0
Silica fume (%)	50.0	50.0	50.0	50.0	50.0	50.0
Silane[2]	-	-	2.0	1.0	-	-

(continued)

	Ex 3a	Ex 3b	Ex 3c	Ex 3d	Ex 3e	Ex 3f
Surfactant[3]	-	-	-	-	1.5	-
Total	100.0	100.0	100.0	100.0	100.0	100.0
[1] ex BASF Corporation; [2] Gamma-aminopropyltriethoxysilane; [3] Sodium-2-ethylhexysulphate (38% aqueous solution)						

[0076] A series of sand tests were then conducted to study the effect of addition of 0.5% BOS of the different silica fume (SF X) slurry compositions on the strength of a mixture of 70% reclaimed sand A and 30% new sand bonded with FENOTEC® 888 and FENOTEC® H20. The results are given in the following tables 5b to 5d.

Table 5b

	Control 1	Control 2	Ex 3a	Ex 3c	Ex 3e	Ex 3f
Water Addition (BOS)	-	0.25%	-	-	-	-
Tensile Strength[1]						
½ hour	20	19	22	19	21	22
1 hour	28	27	35	33	31	34
4 hour	51	51	56	50	50	52
24 Hr	64	66	68	71	70	67
Bench Life (min)	6½	6½	6½	6½	6½	6½
Strip Time (min)	12	11½	10½	11	11	10½
[1]Ambient temperature 21°C; relative humidity 42-65%; sand temperature 19 °C.						

[0077] The results again show that the use of a slurry containing silica fume is advantageous since all of the compositions gave rise to a higher final tensile strength compared to the controls. The addition of a suspension agent (Ex 3a) or a suspension agent and a silane (Ex 3c) or a suspension agent and a surfactant (Ex 3e) also appeared to slightly modify the strength of the resulting products, since Example 3a had highest tensile strength at 1 hour and 4 hours, and Example 3c had the highest tensile strength at 24 hours.

Table 5c

	Control 2	Ex 3a	Ex 3c	Ex 3e
Water Addition (BOS)	0.25%	-	-	-
Tensile Strength[1]				
½ hour	18	26	24	21
1 hour	33	33	34	34
4 hour	45	52	49	43
24 Hr	53	66	68	69
Bench Life (min)	6	6	6	6
Strip Time (min)	10	9½	9½	9½
[1]Ambient temperature 21 °C; relative humidity 42-65%; sand temperature 19°C.				

[0078] The results show that the final strength performance of a silica fume slurry with suspension agent was improved by the addition of a silane (Ex 3c) or a surfactant (Ex 3e) to the slurry.

Table 5d

	Control 1	**Control 2**	**Ex 3a**	**Ex 3b**	**Ex 3f**
Water Addition (BOS)	-	0.25%	-	-	-
Tensile Strength[1]					
½ hour	20	21	24	21	19
1 hour	26	28	29	30	35
4 hour	51	55	58	44	54
24 Hr	58	59	65	60	65
Bench Life (min)	6½	6	6½	6½	6½
Strip Time (min)	11	11	10	10	10
[1] Ambient temperature 21 °C; relative humidity 42-65%; sand temperature 19°C.					

[0079] The table above shows that reducing the level of the attapulgite suspension agent (Attagel® 50) (Ex 3b compared to Ex 3a), and totally removing the suspension agent (Ex 3f compared to Ex 3a) reduces the initial rate of strength development as seen by comparing the 30 minute strengths. However, as shown by Example 3f, the absence of Attagel® has no effect on the final tensile strength at 24 hours, or on the bench life and strip time. The presence of a suspension agent may not have a significant effect on performance of the silica fume slurry in the laboratory, but it will be expected to have significant additional benefits in commercial / industrial applications, as it reduces the tendency for the slurry to settle out of solution and hence reduces the need for extensive re-mixing prior to use.

Example 4 - Grades of Silica Fume

[0080] The performance of two grades of silica fume (SF X and SF Y) were compared by preparing two silica fume slurries (50% silica fume, 0.5% Attagel® 50, 49.5% water) and testing their strength performance on a mixture of 70% reclaimed sand A and 30% new sand bonded with FENOTEC® 888 and FENOTEC® H20. The results are given below in table 6

Table 6

	Control 1	**Control 2**	**Ex 4a (SF X)**	**Ex 4e (SF Y)**
Water Addition (BOS)	-	0.25%	-	-
Tensile Strength[1]				
½ hour	18	18	20	18
1 hour	27	28	35	31
4 hour	43	46	48	46
24 Hr	66	63	65	63
Bench Life (min)	6	6	5½	5½
Strip Time (min)	12½	12	11	11
[1] Ambient temperature 21°C; relative humidity 42-65%; sand temperature 19°C. The results show that the two grades of silica fume have very similar performances, both showing improved initial rate of strength development compared to the two controls.				

Example 5 - Increased Reclaimed Sand Levels

[0081] The effect of a 0.5% addition of silica fume (SFX) slurry (50% solids, 0.5% Attagel 50®, 49.5% water) on increased reclamation levels was studied by increasing the proportion of reclaimed sand C to new sand bonded with

FENOTEC® 888 and FENOTEC® H20 as detailed below in tables 7a and 7b.

Table 7a

	Control 2	**Ex 5a**	**Ex 5b**	**Ex5c**	**Ex 5d**
Reclaimed Sand	70%	70%	75%	80%	85%
New Sand	30%	30%	25%	20%	15%
Water Addition	0.25%	-	-	-	-
Tensile Strength[1]					
½ hour	5	6	5	6	5
1 hour	16	18	17	20	14
4 hour	33	46	39	40	43
24 Hr	57	68	68	63	59
Bench Life (min)	6	6	7	7	7
Strip Time (min)	21	20	21	20½	21
[1]Ambient temperature 19°C; relative humidity 38-48%; sand temperature 18°C.					

Table 7b

	Control 4	**Control 5**	**Control 6**	**Ex 5e**	**Ex 5f**
Reclaimed Sand	70%	75%	80%	75%	80%
New Sand	30%	25%	20%	25%	20%
Water Addition	-	-	-	-	-
Tensile Strength[1]					
½ hour	5	4	3	10	11
1 hour	17	17	13	19	20
4 hour	37	29	34	43	38
24 Hr	72	58	58	61	57
Bench Life (min)	6½	6	5½	6½	6
Strip Time (min)	23	22½	22	18½	18
[1] Ambient temperature 19°C; relative humidity 38-48%; sand temperature 18°C.					

[0082] The results shown in Tables 7a and 7b suggest that as a result in the improved strength and rate of strength development, the level of reclamation i.e. use of reclaimed sand can be increased from 70% to 80% with an addition of silica fume (slurry). One minor negative observation arising from the increased reactivity from the addition of silica fume was a slight reduction in the ultimate (24 hour) strengths, particularly noticeable on the above tests on high alkalinity sand (Foundry C).

Example 6 - Alternative Ester Hardened Resin Grade

[0083] The effect of a 0.5% addition of silica fume (SF X) slurry (50% solids, 0.5% Attagel 50®, 49.5% water) on a mixture of 70% reclaimed sand A and 30% new sand bonded with FENOTEC® 810 (mixed sodium/potassium hydroxide based resin) was studied as detailed below in table 8

Table 8

	Control 1	**Control 2**	**Ex 6**
Water Addition	-	0.25	-
Tensile Strength[1]			
½ hour	5	8	10
1 hour	21	22	24
4 hour	56	53	74
24 Hr	61	62	76
Bench Life (min)	7½	7½	7
Strip Time (min)	22½	19	18½
[1] Ambient temperature 19-21 °C; relative humidity 30-50%; sand temperature 19°C.			

[0084] The results showed that compared to the controls, the addition of a silica fume slurry improved the rate of strength development and ultimate strength of a mixture rebonded with a mixed sodium/potassium hydroxide based ester hardened resin, similar to improvements shown in earlier examples when using a potassium hydroxide based resin.

Example 7 - Carbon Dioxide Gassed Resin Binder

[0085] The effect of a 1% addition of silica fume (SF X) slurry (55% solids, 0.5% Attagel 50®, 44.5% water) on mixture of 50% reclaimed sand A and 50% new sand bonded with ECOLOTEC® 750 was studied as detailed below in table 9.

Table 9

	Control 1	**Control 7**	**Ex 7**
Water Addition	-	0.45	-
Tensile Strength[1]			
5 minutes	22	18	21
1 hour	28	24	36
24 Hr	27	24	35
7 Day	26	20	37
[1]Ambient temperature 20°C; relative humidity 55%; sand temperature 19°C.			

[0086] The results show that the addition of a silica fume slurry improved the rate of strength development and ultimate strengths of reclaimed sand rebonded with a carbon dioxide hardened alkaline phenolic resin, compared to the two controls,.

Example 8 - Sodium Silicate Reclaimed Sand

[0087] The effect of a 0.3% addition of silica fume (SF X) slurry (55% solids, 0.5% Attagel 50®, 44.5% water) on mixture of 50% reclaimed sand D and 50% new sand bonded with ECOLOTEC® 750 was studied as detailed below in table 9.

Table 10

	Control 1	**Ex 8**
Water Addition	-	-
Tensile Strength[1]		

(continued)

	Control 1	Ex 8
5 minutes	16	20
1 hour	31	46
24 Hr	12	12
7 Day	17	27
[1] Ambient temperature 20°C; relative humidity 61 %; sand temperature 19°C.		

[0088] The results show that the addition of a silica fume slurry improved the rate of strength development and ultimate strengths of reclaimed sodium silicate sand rebonded with a carbon dioxide hardened alkaline phenolic resin, compared to the control,. Although the invention should not be construed as being limited by any particular theory, the inventors postulate that the beneficial effect of the silica fume is due to its reactivity with potassium and/or sodium hydroxide residues in the reclaimed sand, to form potassium and/or sodium silicate hydrate gel. Based on this assumption, the performance of silica fume in alkaline reclaimed sand depends on the addition level of silica fume and the properties of the reclaimed sand i.e. the type and composition of alkaline material in the sand and overall level (alkalinity). The exact relationship between the addition levels of silica fume and the alkalinity content has yet to be determined. However, it has been observed that whilst falling within defined ranges, the optimum addition levels of silica fume may vary depending upon sand and binder type.

Claims

1. A foundry moulding composition for the manufacture of foundry moulds and cores, comprising
   sand;
   a binder; and
   silica fume and/or a silica fume substitute,
   wherein the sand comprises reclaimed sand comprising alkaline binder residues.

2. The composition of claim 1, wherein the alkaline binder residues are selected from one or more of potassium silicate, sodium silicate, potassium carbonate (potash), sodium carbonate (soda), sodium hydroxide, potassium hydroxide, sodium acetate and potassium acetate.

3. The composition of claim 1 or claim 2, wherein the silica fume and/or silica fume substitute is present in an amount of at least 0.1% by weight of sand.

4. The composition of any one of the preceding claims, wherein the particle size (d90) of the silica fume and/or silica fume substitute is no more than 50μm.

5. The composition of any one of the preceding claims, wherein the SiO_2 content of the silica fume or the silica fume substitute is at least 75wt%.

6. The composition of any one of the preceding claims, wherein the reclaimed sand has a pH of from 8 to 12.

7. The composition of any one of the preceding claims, wherein the silica fume substitute is present and is Rice Husk Ash (RHA).

8. The composition of any one of the preceding claims, wherein the sand comprises at least 50wt% reclaimed sand.

9. A method for preparing a foundry moulding composition, comprising mixing sand, a binder and silica fume and/or a silica fume substitute, wherein the sand comprises reclaimed sand comprising alkaline binder residues.

10. The method of claim 9, wherein the alkaline binder residues are selected from one or more of potassium silicate, sodium silicate, potassium carbonate (potash), sodium carbonate (soda), sodium hydroxide, potassium hydroxide,

sodium acetate and potassium acetate.

11. The method of claim 9 or 10 comprising an additional initial step of reclaiming sand that is bonded by an inorganic or mixed organic-inorganic binder.

12. The method of any one of claims 9 to 11, wherein the inorganic or mixed organic-inorganic binder is an ester-cured or a CO_2 gas-cured binder.

13. The method of any one of claims 9 to 12, wherein the inorganic or mixed organic-inorganic binder is a sodium silicate binder or an alkaline phenolic binder.

14. A method for making a foundry mould or core comprising preparing the foundry moulding composition of any one of claims 1 to 8;
optionally adding a chemical hardener;
forming the composition into a desired pattern or shape; and
curing the binder.

15. The method of any one of claims 9 to 14, wherein the silica fume and/or the silica fume substitute is provided in the form of a slurry.

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EUROPEAN SEARCH REPORT

Application Number
EP 10 25 0128

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B22C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	8 October 2010	Lombois, Thierry

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EUROPEAN SEARCH REPORT

Application Number
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