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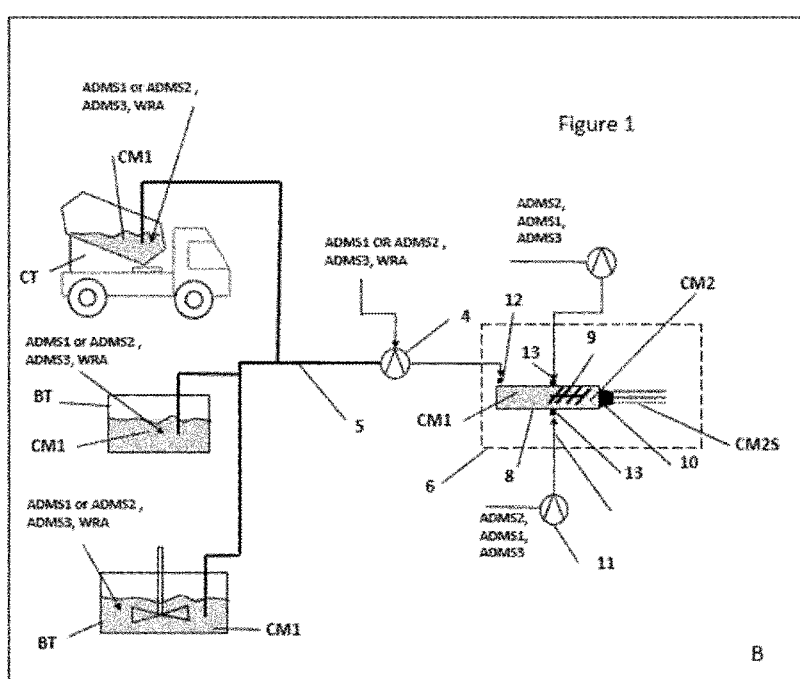
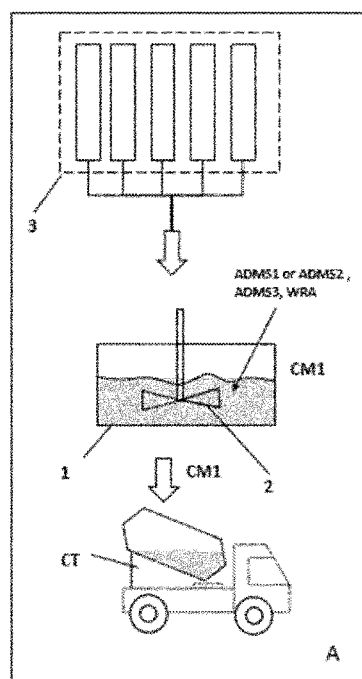


FIGURE 1

(57) Abstract: The present invention relates to a new construction material 3D printing method for production of a printable construction material (CM2S) which is a ready-mix concrete or mortar containing water, binder, sand, small and medium sized aggregates as well as various additives, and its transport to jobsites equipped with 3D printing (6,8) for placing the printable construction material (CM2S).

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READY-MIX CONSTRUCTION MATERIAL 3D PRINTING METHOD

DESCRIPTION

5 Technical field of the invention

The present invention relates to a new construction material 3D printing method for production of a printable construction material which is a ready-mix concrete or mortar containing water, binder, sand, small and medium sized aggregates as well as various additives, and its transport to jobsites equipped with
10 3D printing for placing the printable construction material.

State of the art

Traditionally, construction materials like concrete are placed or casted using fluid material that is poured into a form, either *in situ* on jobsites, or in precast
15 operations. The concrete is then maintained in the form until some level of strength is achieved (between some hours and 14 days depending on the concrete mix designs and admixtures systems). The form is then removed, and the concrete continues to cure and harden.

Modern industrial requirements in terms of productivity, continuous production,
20 or reduction of manipulation costs are driving a shift in the way construction materials (e.g., concrete or similar) are placed on job sites. Such is typically the case for concrete extrusion, 3D printing or the same, that enable to place the concrete without using a form, avoiding the immobilization of expensive forms or frames.

This new industrial trend requires however a much more sophisticated control
25 of the concrete rheology at different moment of the production chain (mixing the concrete, transporting the concrete, adding the concrete to the continuous production line, extruding the concrete through a die), to finally obtain a fresh concrete shape that will sustain its own weight or the weight of additional layers in the case of 3D printing without dimensional changes with time (e.g., collapsing) and
30 rapidly develop strength. Perhaps this is why most of 3D printing solutions proposed today are limited to special mortars containing only sand and no mineral aggregates larger than 2 mm, prepared from dry premixes at the 3D printing and mixed with water and other ingredients at the 3D printing jobsites.

The production rate, expressed as linear meters of extruded concrete placed by hour, of volume extruded by hour, is a critical factor for economic efficiency of the placing process. There is an important number of patents and patent applications related to the topic.

5 Finally, an industrial process must be able to print concrete mix designs containing medium to large size aggregates (size >4 mm) and not only mortars containing aggregates of maximum size from 2-4 mm, using conventional ready-mix preparation techniques in a ready-mix plant and transporting the concrete using ready-mix trucks.

10 Using conventional concrete manufacturing in specific plants and transporting the concrete on the job site presents the key advantage to avoid having cement silos, sand or aggregates silos, water and admixtures silos on the job site and all the issues refilling these silos and the printing works progresses.

US 5123831 for instance describes a concrete extrusion device for concrete
15 manufacturing of hollow shapes parts. The patent does not however provide any information regarding the mix designs of the concrete or the technology used to ensure the self-mechanical sustained material once leaving die. The concrete used is a zero-slump concrete that remains at constant fluidity/viscosity all through the extrusion machine.

20 The RILEM (A. Perrot et al., RILEM Technical Letters. (2018) 3: 91-97) published a review on various technologies addressing the extrusion of concrete and cites the use of rheology modifying agents with no details on dosage, type of chemicals or details on concrete mix designs.

EP3626420B1 describes a system to produce parts using spray concrete but
25 provide no details on the concrete mix designs.

EP2954133B1 describes an apparatus and method for vertical slip forming of concrete structures, using a movable slip for continuous production of concrete parts. The document does not provide any information on the mix design of the stiffening of the concrete.

30 EP3421201B1 describes a cementitious and mortar formulation for extrusion or 3D printing containing mineral fillers and slag additions on top of the conventional concrete ingredients (cement, water, sand). The patent limits itself to aggregates size smaller than 1 mm and uses a combination of PCE, viscosity modifiers and

shrinkage reduction agents. Furthermore, EP3421201B1 describes very high water/cement ration (over 0.6) that will limit the maximum available strength of the hardened mortar. Finally, EP3421201B1 provides with a constant mortar formulation throughout the extrusion system, with no modification of the rheology
5 during the extrusion/3D printing process.

WO2011066192A1 also describes a mortar or concrete formulation for extrusion, containing amongst other organic based fibers (cellulose fibers and polyvinyl alcohol fibers), use of rheology modifying agents and other admixtures (strength enhancing amines and other strengtheners, dispersants, water reducers,
10 superplasticizers, water binding agents, viscosity modifiers, corrosion inhibitors, pigments, wetting agents, water soluble polymers, etc.). As previously, the composition of the concrete and the various admixtures remain constant throughout the extrusion process. This technology has important limitations in terms of final strength as all admixtures need to be included into the concrete/mortar mix design
15 that is fed to the extrusion. The technology does allow for metallic fibers.

WO2019089771A1 similarly describes a cementitious mix design containing only sand as aggregates and organic fibers.

EP3558679B1, the document describes a method and a device for 3D printing of concrete yet does not provide any examples or details of concrete mix designs.

20 EP3664980 B1 describes a 3D printing technology using mortars whereas a set acceleration additive is added in a mixer that is part as the printer head and is limited to mortars containing aggregates up to 2 mm. Adding a set accelerator in the printer head does not solve the problem of controlling the rheological properties of the material to be printed and expected the concrete to set before a second layer is
25 added to the initially printed layer.

EP3260258B1 describes a methodology to modify the rheology of the mortar composition during the 3D printing process, by adding to the mortar a rheology modifier agent in a static mixer located far before the printing nozzle. The rheology modifying agent is selected from starch ether, celluloses ether, water soluble
30 polyacrylamide, casein, and/or Welan gum. The patent only provides examples of mix designs comprising sand as aggregates (no aggregates larger than 2 mm) and does not mention the possible use of fibers (organic, mineral or metallic). High strength can only be obtained by using super high strength cement (Ductal®) as the

water to binder ratio remains quite high in the examples (above 0.45), or strength enhancers, setting accelerators, etc.... It is also clear that using rheology modifying agents has drawbacks as the stiffness of the mortars that can be obtained leaving the nozzle is limited. EP3260258B1 specifies that the yield/shear stress of the stiffened mortar obtained after adding the rheology modifier agent has to be located between 600 and 4 000 Pa, that would be far too low to stiffen a concrete containing aggregates.

Finally, Gosselin, C., Duballet, R., Roux, P., Gaudillière, N., Dirrenberger, J. and Morel, P. (Large-scale 3D printing of ultra-high performance concrete – a new processing route for architects and builders. *Materials & Design*. (2016) 100, 102-109), describes a 3D printing equipment that provides a mixer, a gantry and a printer head to which a set accelerator additive and a rheology modifier admixture can be added to better control the rheology and setting time of the freshly printed material. The method is limited to the use of mortars with only sand type aggregates with sizes <4 mm) and presents the disadvantage to store and mix all mortars constituent on the jobsite.

As a conclusion, the prior art does not disclose any production process that describes the use of a large variety of mortar or concrete industrial mix designs prepared in ready-mix plants and transported to the jobsite, containing optionally metallic fibers and using aggregates larger than 4 mm. Furthermore, the prior art does not disclose a robust technology to radically transform a fluid concrete, to a very stiff concrete once leaving the printing nozzle of the extrusion die without using accelerators or viscosity modifiers, allowing the printing material to maintain its geometrical extruded dimensions over time and setting before the next layer is applied by 3D printing nozzle.

Description of the invention

The present invention describes a robust industrial process to use construction material prepared in ready-mix plants, presenting a wide range of mix-designs with water to binder weight ratio ranging from 0.4 to 0.65 and transported to the jobsites using conventional concrete transportation trucks. At the jobsites equipped with 3D printing, the construction material is directly used from the concrete truck or dumped into a hopper to be pumped to the printing head of the 3D printing equipment. Since

the construction material must be fluid yet very stable (absence of aggregates segregation) during the transportation and during the pumping to the printing head that can take many hours, special admixtures combinations are used as part of the solution to the problem to transform a stable fluid concrete mix design into a stiffened construction material once it leaves the printer head to ensure dimensional stability of the deposit material.

An object of the present invention is therefore a 3D printing industrial production method for fresh construction material containing a hydraulic binder, said method comprising the following steps:

- 10 a) Preparing a ready-mix construction material (CM1) in a concrete-type mixer or concrete batching plant or local static concrete mixer or concrete truck, from the following mix design:
 - Binder (250 to 700 kg/m³);
 - Water (100 to 455 kg/m³);
 - 15 - Sand (400 to 1100 kg/m³);
 - Aggregates having a size from 4-16 mm, preferably from 4-12 mm, (400 to 1200 kg/m³);
- b) Transporting CM1 obtained in a) from the concrete-type mixer or concrete batching plant or local static concrete mixer or concrete truck, to a jobsite equipped with a 3D printing equipment;
- 20 c) Optionally transferring CM1 into a buffer container at the jobsite;
- d) Moving the CM1 towards a printer head of the 3D printing equipment;
- e) Adding a first (ADMS1) and/or second (ADMS2) admixture system to CM1, uphill from a nozzle of the printer head of the printing equipment yet at a distance located from 0.2 m to 4 m from the nozzle, to obtain a second construction material (CM2), provided that:
 - ADSM1 is added in step e) when ADMS2 is added in step a), b), c) and/or d);
 - ADSM2 is added in step e) when ADMS1 is added in step a), b), c) and/or d); or
 - ADMS1 and ADMS2 are both added in step e); and
- 25 wherein ADMS1 comprises at least a high molecular weight, non-ionic water-soluble component, and is dosed at a range from 0.0001 to 0.5 weight% of the binder content;

wherein ADMS2 comprises at least a polymerized system containing a conjugated or aromatic/non-aromatic, homocyclic/heterocyclic, mono-ring, bi-ring or poly-ring system that contains solubilizing functional groups, and is dosed at a range from 0.05 to 5 weight% of the binder content, preferably from 0.1 to 3 weight% of the binder content, more preferably from 0.60 to 2% weight% of the binder content;

f) Extruding CM2 obtained in e) through the nozzle of the printed head of the printing equipment;

g) Recovering the stiffened construction material (CM2S) after the nozzle of the printed head of the printing equipment.

10 Experimental tests have shown that choosing to add first ADMS2, respectively ADMS1, to the construction material CM1 and then stiffen CM1 adding ADMS1, respectively ADMS2, has no effect on the rheology and printing quality of CM2 and CM2S on the resistances of the hardening construction material printed.

ADMS2 and ADMS1 can be thus jointly or separately added using pumping and dosing devices to CM1 in the printer head using one or 2 inlet(s) (13). Adding both ADMS2 and ADMS1 directly in the printer head does not impact the rheology and the quality of the printed material CM2S. For example, ADMS2 is added to CM1 in step a), b), c) and/or d), and ADMS1 is added in step e). For example, ADMS1 is added to CM1 in in steps a), b), c) and/or d) and ADMS2 is added in step e). For example, ADMS2 is added to CM1 in step c) and/or d), and ADMS1 is added in step e). For example, ADMS1 is added to CM1 in in steps c) and/or d) and ADMS2 is added in step e).

According to a particular embodiment of the present invention, and irrespective if ADMS2 or ADMS1 is selected to be the first admixture system added to CM1, the 3D printing industrial production method further comprises (i) a third admixture system (ADMS3) which is added to CM1 in step a), b), c), d) and/or e); and/or (ii) a water reducing agent (WRA) which is added in step a), b), c) and/or d); and wherein ADMS3 comprises further components chosen from the group consisting of setting or hardening accelerators, pigments, air entrainers, anti-freezing agents, retarders, and any mix thereof, and is dosed at a range from 0.1 to 3,5 weight% of the binder content.

According to a particular embodiment of the method of the present invention, CM1 further comprises in steps a) or d) at least one component among: foam,

lightweight aggregates, organic, mineral and metallic fibers or any combination thereof, fillers, micro or nano silicates, pigments, silica fume, activated glass, pozzolans, granulated slag, fly ash, activated clay, set accelerator, air entrainer, shrinkage reducer, activators, self-curing admixture systems. For example, CM1
5 further comprises mineral and/or metallic fibers.

According to a particular embodiment of the method of the present invention, the binder is a cement selected from ordinary Portland cement (CEM, CEM II CEM III CEM IV), or cement-free binder containing slag, fly ash, natural pozzolans, micro silica, activated clay, limestone, calcium oxide, calcium chloride, or any combination
10 thereof and the admixture system.

According to a particular embodiment of the method of the present invention, ADMS1 is a high molecular weight, non-ionic water-soluble component selected from polyethylene glycol (PEG) or polyethylene oxide (PEO), polyamine, or a mixture thereof. ADMS1 has a solid content comprised from 0.0001 (1e-4 wt%) to 2
15 or 0.5 weight% of the binder content, preferably from 0.001 to 2 weight% or 0.001 to 1 weight% of the binder content, more preferably from 0.001 to 0.003 weight% of the binder content. For example, the PEG consists of repeating dimethyl ether chains with hydroxyl-terminated groups, $\text{OH-CH}_2\text{-(CH}_2\text{-O-CH}_2\text{)}_n\text{-CH}_2\text{-OH}$, which solid content is comprised between 0.001 weight% and 2 weight% or 0.001
20 weight% and 1 weight% of binder content. For example, the polyamine is a copolymer of polyamine that can have low to high molecular weight range and a low to high cationic charge which solid content is comprised between 0.0001 weight% (1e-4 wt%) and 0.5 weight% of binder content, preferably from 0.001 weight% and 0.003 weight% of the binder content.

25 According to a particular embodiment of the method of the present invention, ADMS2, which react with ADMS1 to transform CM1 into CM2, comprises at least a polymerized system that can be chemistry containing conjugated or aromatic/non-aromatic, homocyclic/heterocyclic, mono-ring, bi-ring or polyring system (polyring equal two or more rings of any size) selected from benzene, triazine, naphthalene, anthracene, pyrene, phenanthrene, isoquinoline, chrysene, that contains
30 solubilizing functional groups such as sulfate, carboxylic acid, nitrates.

According to a particular embodiment of the method of the present invention, ADMS2 is dosed to the construction material printed by the 3D printing (CM2S) in a

range from 0.05 to 5 weight% of the binder content, preferably from 0.1 to 3 weight% of the binder content, more preferably from 0.60 to 2% weight% of the binder content.

According to a particular embodiment of the method of the present invention,
5 the solid weight ratio between ADMS1 and ADMS2 ranges from 1/2000 to 1/200 in the CM2 or CM2S construction material.

Another object of the present invention is also the use of a CM2S obtained by a method according to the present invention, to continuously produce rails, plates, barriers, rods, bars, hollow pipes, roof tiles or the same; or to deposit by 3D printing
10 successive layers to form walls, piles, pillars or the same.

The important stiffening expressed by a yield shear value of the CM2S for instance can be measured, as will be seen in the examples below, using a shear vane, showing the ability to maintain shape after extrusion of the construction material after adding ADMS1, is due to a chemical strong interaction between
15 ADMS2 and ADMS1. The reaction in the form a polymerization produces a 3D connected net that immediately reduces the fluidity of the construction by a matrix effect and provides stiffness property that allow the extruded/printed material to support its own weight without deformation, keeping stable dimensions and geometries of parts/layers from the nozzle/die.

20 The stiffening effect is a result of the electrostatic (CH- π) interactions between the ADMS1 (e.g. PEO/PEG) and ADMS2 (e.g. naphthalene ring in the poly β naphthalene sulfonate) where the electron density is shifted from the aromatic π system to the ethylene protons of the ADMS1. The high molecular weight of the ADMS1 and the polymeric network of the ADMS2 enhances the bonding strength
25 and thus formation of a supramolecular network which gives the increased in the yield stress and thus results in the observed stiffening reaction.

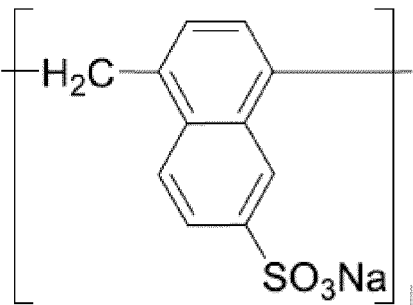
Definitions

Accelerator	To increase the rate of hydration of hydraulic cement, shorten the time of setting and increase the rate of early strength development. This allows to build up as the material would withstand pressure from the upper layers.
Admixture	Chemical admixtures used to modify or improve concrete's properties in fresh and hardened state. These could be air entrainers, water reducers, set retarders, accelerators, stabilizers, superplasticizers and others.

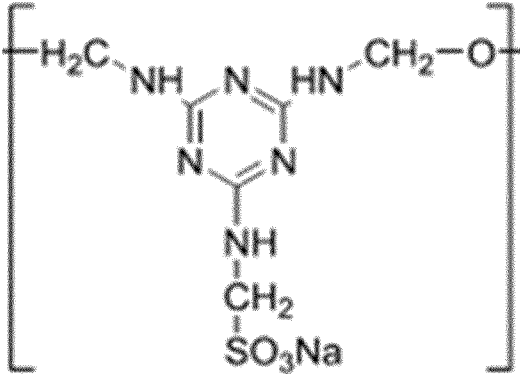
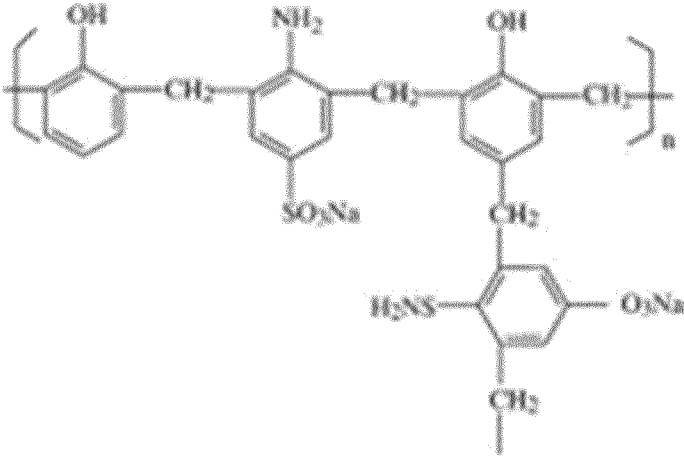
Air entrained	Total volume of air entrained in the concrete by the air entrainer.
Aggregates	Aggregates are inert granular materials such as sand, gravel, or crushed stone that, along with water and Portland cement, are an essential ingredient in concrete.
Aspect ratio	The ratio of length to width of individual pieces of fiber.
Binder	Mineral material with hardening properties including cements or pozzolans or any mix of the two, ground granulated blast furnace slag (GGBS), fly ash, microsilica limestone filler or any mix thereof
Binder content or total binder content	Sum of the respective weights of all types of binders present in a given mix design
Cement	Binder that sets and hardens and bring materials together. The most common cement is the ordinary Portland cement (OPC) and a series of Portland cements blended with other cementitious materials.
Coarse Aggregates	Manufactured, natural or recycled minerals with a particle size greater than 4mm and a maximum size lower than 40mm
Concrete	Concrete is primarily a combination of hydraulic binder, sand, fine and/or coarse aggregates, water. Admixture can also be added to provide specific properties such as flow, lower water content, acceleration...
Consistency	Degree of wetness of concrete.
Construction materials	Any materials that can be used to build construction element or structure. It includes concrete, masonries (bricks – blocks), stone, ICF...
Fiber	Material used to increase concrete's structural performance. Fibers include: steel fibers, glass fibers, synthetic fibers and natural fibers.
Fresh construction material	State of a construction material (e.g. concrete) from the moment water is added to the moment where it begins to set, having plasticity allowing it to be moved, deformed and/or molded, although this is not a permanent factor.
Fine Aggregates or sand 0-4	Manufactured, natural or recycled minerals with a particle size typically greater than 0 mm and a maximum size lower than 4 mm
Flexural strength	Is the strength measured on 3 points bending tests (notched prismatic samples 500 mm x 150 mm x 150 mm) according to norm EN 14651
High-strength concrete	The strength of these type of concrete is higher than 41 Mpa.
Lightweight aggregate	Any aggregate with a dry loose bulk density of less than 1200 kg/m ³ .
Mechanical resistance	Mechanical resistance of the fibers before rupture.

Mineral Addition	Mineral admixture (including the following powders: silica fume, fly ash, slags) added to concrete to enhance fresh properties, compressive strength development and improve durability.
Natural Pozzolan	Aluminosilicate material of volcanic origin that reacts with calcium hydroxide to produce calcium silicate hydrates or CSH as known in Portland cement hydration.
Normal strength concrete	The strength of these type of concrete will vary from 10 Mpa to 40 Mpa. The normal strength concrete has an initial setting time of 30 to 90 minutes that is dependent on the cement properties and the weather conditions of the construction site.
Ordinary Portland cement	Hydraulic cement made from grinding clinker with gypsum. Portland cement contains calcium silicate, calcium aluminate and calcium ferroaluminate phases. These mineral phases react with water to produce strength.
PCE	PCE are Polycarboxylic Acid Co-Polymers used as a class of cement and concrete admixtures, and are comb type polymers that are based on: a polymer backbone made of acrylic, methacrylic, maleic acid, and related monomers, which is grafted with polyoxyalkylene side-chains. The grafting could be, but is not limited to, ester, ether, amide or imide.
Silica fume	Source of amorphous silicon obtained as a byproduct of the silicon and ferrosilicon alloy production. Also known as micro silica.
Slump	The consistency of fresh concrete before it sets – the higher the slump, the more fluid the concrete is. Measured in mm.
Stiffness	Ability to maintain the shape after extrusion without flowing or collapsing. Characterized by a shear vane value or a reduced slump, prior to the setting time of the fresh concrete. A stiffened concrete remains soft and can plastically be deformed provided the stress is high enough.
Strength development – setting / hardening	The setting time starts when the construction material changes from plastic to hard and strong. In the harden stage the material cannot be poured or moved anymore. After this phase the strength development corresponding to the hardening of the material
Structural applications	A construction material is considered as structural as soon as the compressive strength of the material is greater than 25 MPa
Superplasticizers	Superplasticizer relates to a class of chemical admixture used in hydraulic cement compositions such as Portland cement concrete having the ability to highly reduce the water demand while maintaining a good dispersion of cement particles. In particular, superplasticizers avoid particle aggregation and improve the rheological properties and workability of cement and concrete at the different stage of the hydration reaction.

Total binder	Is the sum of all cementitious components (cement, flay ash, slag, silica fume, etc.)
w/b	Total free water (w) mass in Kg divided by the total binder mass in Kg
WRA	Water reducing agents (WRA) relates to various type of plasticizers or superplasticizers, with the ability to reduce the water demand in a cementitious mixture, thus increasing the final strength while maintaining a geed workability.
Workability	The workability of a material is measured with a slump test (Table A: slump)
CM1	Construction material according to the invention at step A
CM2	Construction material according to the invention containing both ADMS2 and ADMS1
CM2S	Stiffened construction material at the outlet of the print nozzle

Admixture/additive Name	Structural Examples
PNS: Polynaphthalene sulfonate	 The chemical structure shows a repeating unit of Polynaphthalene sulfonate (PNS) enclosed in large square brackets. Inside the brackets, a naphthalene ring system is depicted. A methylene group (H₂C) is attached to the 1-position of the naphthalene ring. A sulfonate group (SO₃Na) is attached to the 4-position of the naphthalene ring. The brackets indicate that this is a repeating unit of a polymer.

PCE: Polycarboxylate ether/ester Superplasticizer	The structure shows a copolymer of two units, 'a' and 'b', connected by a central chain. Unit 'a' is a methacrylate derivative with a sodium carboxylate group (ONa) and a methyl group (CH₃). Unit 'b' is a methacrylate derivative with a methyl group (CH₃) and a polyether side chain. The polyether side chain consists of a methylene group (CH₂) connected to a polyoxyethylene chain (CH₂-CH₂-O-CH₂-CH₂-O-CH₃) with a subscript 'n = 10'. HPEG PCE
Lignosulfonate (LS) Plasticizer	The structure shows a lignosulfonate molecule. It features a central carbon atom bonded to a hydroxyl group (HO), a methoxy group (O-CH₃), a sodium sulfonate group (Na⁺ SO₃⁻), and a phenyl ring. The phenyl ring is further substituted with a methoxy group (O-CH₃) and a propyl chain (CH₂-CH₂-CH₂-SO₃H).

Polymelamine sulfonate (PMS)	
SFS: sulfanilic acid–phenol–formaldehyde	

Relevant information related to Norms and normative tests regarding measurement of concrete’s consistency is described in A and B Table C

5 Table A- Consistency of concrete (slump) with respect to EN (European) and FR (French) Norms and normative tests.

EN 12350-2		NF P 18-305	
Consistency	slump [mm]	Consistency	slump [mm]
S1	10 to 40	Stiff	0 to 40

S2	40 to 90	Plastic	50 to 90
S3	100 to 150	highly plastic	100 to 150
S4	160 to 210	fluid	> 160
S5	> 220	Very fluid	> 210mm

Table B– Consistency of concrete (flow) with respect to EN 12350-8 (European) Norms

EN 206-1	
category	Flow [mm]
SF1	550 -650
SF2	660 -750
SF3	760 – 850

5 Table C– Consistency stiffness of the concrete measure by hand shear vane tester and visual assessment. Tester equipped with a modified 100mm x 50mm blade.

Shear vane value		
Extrudability assessment	Shear value (kPa)	Concrete consistency
non-extrudable	0-20	Fluid
Extrudable	20-50	Low or no slump/solid/soft
non-extrudable	> 50	Dry/very stiff/hard

Brief description of the figures

10 Figure 1 represent (A) a schematic representation of a concrete mixing plant (B) a schematic representation of the invention device that can be used to carry out the claimed invention, presented to better understand the invention.
Figure 2 shows the evolution of the calorimetric measurements of CM1 containing different dosages of ADMS1.

15

EXAMPLES

EXAMPLE 1: PROPERTIES OF A CONSTRUCTION MATERIAL CM1 + ONLY ADMS1 (not part of the claimed invention)

We measured experimentally, using the yield shear vane, the level of stiffening that can be obtained on using ADMS1 only (with no previous additions of ADMS2 in CM1), added to Test-CM1 (prepared according to the mix design below) close or in the printer head. The Table D1 shows the results obtained with various dosages.

- 5 Table D2 also shows the effect of the dosage of ADMS1 on the setting time of test CM1 using an automatic calorimetry, with the following mix design: CEM I 52,5R 450 kg, 0-4 round sand 769 kg/m³ and 4-8 round aggregate 846 kg/m³ and water W/B=0.50.

- 10 Table D1 evolution of the yield shear measured on Test-CM1 as a function of the dosage of ADMS1 in weight percent of the binder (cement)

ADMS1 dosage (weight % binder content)		Initial slump flow (mm) at 1-3min after mixing	Initial Shear (kPa) after 1- 3min mixing
0		480	10
6.67e-4	Average regular dosage for 3D printing	470	12
2.00e-3	3 times regular dosage	470	10
6.67e-3	10 times regular dosage	470	13
6.67e-2	100 times regular dosage	470	10

Table D2: Evolution of the setting time of the Test-CM1 with the dosage of ADMS1

ADMS1 dosage (% binder content)	Setting time (h)	24h compressive strength on cube (MPa)
0	>4h	20.4
6.67e-4	>4h	19.5
2.00e-3	>4h	21.0
6.67e-3	>4h	19.0
6.67e-2	>4h	20.8

- 15 ADMS1 alone does not yield any setting acceleration of CM1 and having a pseudo-dispersant effect will rather decrease than increase the viscosity of

CM1. Therefore ADMS1 and ADMS2 individually used in CM1 cannot be considered neither as accelerating agents nor as viscosity increase modifiers, as if used alone, will not satisfy the condition of the shear/extrudability criteria of CM2.

It can be seen from Tables D1 that the additions of ADMS1 alone does not
5 yield any rheology modification of the concrete mix-design, so the printing of CM1 + ADMS1 will not be possible as the concrete will be too fluid as no stiffening is occurring.

In a similar way, it can be seen from Table D2, that the addition of ADMS1 alone does not influence the setting time of the CM1 + ADMS1 over hours even at
10 dosages 100 times higher than those used in the present invention.

Additions of ADMS1 alone does not allow CM1 to be printable, either by increase viscosity (rheology modification) or by reduced setting time (accelerator).

EXAMPLE 2: IMPLEMENTATION OF THE CLAIMED METHOD FOR 15 PRODUCTION OF FRESH CONSTRUCTION MATERIAL

The examples below are provided on a simplified experimental design that considers mainly adding ADMS2 first to CM1 and then adding ADMS1 to CM1. The invention is not limited to examples provided and of course any combination according to the invention is covered. The implementation of the process of the
20 present invention is not limited by the schema presented in figure 1 (A & B).

The mix designs described in tables E and F below were obtained using conventional batching process of concrete well known to the skilled person, in a conventional 500 L capacity mixer, according to the claimed process and figures 1 A and B.

25 The cements used are commercialized cement available in Europe.

The aggregates are calcareous/silica with sized from 4 to 16 mm.

The sand is calcareous/silica based with sizes from 0 to 4 mm.

The lightweight aggregates and sand are obtained from expanded clay or expanded glass, with bulk densities from 150 kg/m³ to 1000 kg/m³.

30 The metallic fibers are characterized by a ratio length to diameter ranking from 20 to 120, with a total length located between 10 mm to 100 mm. The metallic fibers are straight or hooked fibers with tensile strength located between 600 MPa and 4000 MPa and E Modulus located between 185 GPa and 215 GPa

Alternatively, organic fibers or mineral fibers have been as described in EP3307692B1.

3D printing nozzle sizes are ranking from 10 cm² to 150 cm², preferably from 20 cm² to 100 cm² with rectangular, round, square or elliptic shapes, or any other 5 shapes.

The consistency properties were measured according to the details provided in Tables, A, B and C.

The stiffness is measured using hand shear vane tester or visual assessment (ability to maintain shape after extrusion). The strength is measured on standard EN 10 cubes in compression according to norm EN 12390-3.

Table E: examples of mix designs and properties using dense silicates/limestones aggregates and sand

	MD 1	MD2	MD3	MD4	MD5	MD4-1
Main Binder type	Cement	Cement	Cement	Cement	Cement	Cement
Main binder Dosage kg/m ³	400	420	370	450	450	450
Second Binder type	NA	Microsilica	Limestone filler	NA	NA	NA
Second binder dosage (kg/m ³)	NA	48	130	NA	NA	NA
Water kg/m ³	202	215	190	200	202	200
Sand kg/m ³	755	762	736	798	755	798
Large aggregates size	4-8 mm round	4-10mm crushed	4-12mm round	4-8mm round	4-8 mm round	4-8mm round
Large aggregates kg/m ³	906	828	884	878	906	878
Metallic fibers kg/m ³	NA	20	40	NA	NA	NA
Set accelerators (ADMS3) dosage in % of binder content	0%	0%	0	3.05%	1.75%t	0.75%
ADMS2	SFS	PNS	PNS	PNS	SFS	PNS
WRA	0	PCE	PCE	0	PCE	0
ADMS1	PEO/PEG	PEO/PEG	PEO/PEG	PEO/PEG	PEO/PEG	PEO/PEG
ADMS2 dosage as a percentage of total binder	1.20% (5.4kg/m ³)	0.68% (3.18kg/m ³)	0.40% (2.00kg/m ³)	1.00% (4.50kg/m ³)	0.015% (0.67 kg/m ³)	1.00% (4.50kg/m ³)
WRA dosage as a percentage of total binder	0	0.2% (0.94kg/m ³)	0.06% (0.30kg/m ³)	0	0.27% (01.22kg/m ³)	0
First Admixture system added to CM1	ADMS2	ADMS1	ADMS2	ADMS1	ADMS2	ADMS1

Second admixture system added to CM1 to obtain CM2	ADMS1	ADMS1	ADMS1	ADMS2	ADMS1	ADMS2
Consistency of CM1 with the first added admixture system	slump flow between 300-550mm	slump flow between 300-550mm	slump flow between 300-550mm	slump flow between 300-550mm	slump flow SF2	slump flow between 300-550mm
ADMS1 dosage of total binder content	0.0011% (0.005kg/m ³)	0.0014% (0.0065kg/m ³)	0.0011% (0.005kg/m ³)	0.0012% (0.0054kg/m ³)	0.0011% (0.005kg/m ³)	0.0012% (0.0054kg/m ³)
Consistency of CM2	Extrudable, no slump concrete	Extrudable, no slump concrete	Extrudable, no slump concrete	Extrudable, no slump concrete	Non-extrudable	Extrudable, no slump concrete
Shear vane value (KPa)	30	28	42	32	9	34
Strength at 1 day (on cubes)	19.6 MPa	25.2 MPa	27.4 MPa	20.0 MPa	18.6 MPa	21.2 MPa
Strength at 7 days (on cubes)	41.3 MPa	38.0 MPa	37.5 MPa	42.8 MPa	39.3 MPa	40.5 MPa
Strength at 28 days (on cubes)	50.4 MPa	48.0 MPa	46.8 MPa	49.9 MPa	47.2 MPa	47.9 MPa

Table F: Examples of mix designs and properties using light weight aggregates and air entrainer

	MD1-L	MD2-L
Main Binder type	Cement	Cement
Main binder Dosage kg/m ³	360	250
Second binder type	Fly ash	NA
Second binder dosage kg/m ³	200	NA
Water kg/m ³	170	138
Lightweight Sand kg/m ³	120.1	140
Large lightweight aggregates size	2-10mm	NA
Large lightweight aggregates kg/m ³	406.5	0
Air entrainer type	NA	ISOFOAM 6000 From CEMEX Admixtures GmbH
Measured Air content	NA	50%
Metallic fibers	NA	
ADMS2	SFS	PNS
WRA	PCE	PCE
ADMS1	PEO/PEG	PEO/PEG
ADMS2 dosage in weight percentage of binder content	0.40% or 2.24kg/m ³	0.24% or 0.6kg/m ³
ADMS1 dosage in weight percentage of binder content	0.0015% (0.0084kg/m ³)	0.0025% (0.0063kg/m ³)
WRA dosage in % of binder content	0.06% or 0.34kg/m ³	0.30% or 0.75 kg/m ³
First Admixture system added to CM1	ADMS2	ADMS1
Second admixture system added to CM1 to obtain CM2	ADMS1	ADMS2
Consistency of CM1 with the first added admixture system	S4-S5	S4-S5
Other Consistency of CM1 with the first added admixture system	SF1 to SF3	SF1 to SF3
Set accelerators (ADMS3) dosage in % of binder content	0.55%	3.2%
Consistency of CM2	extrudable	extrudable
Strength at 1 days	21 MPa	0.5 MPa
Strength at 7 days	36 MPa	1 MPa
Strength at 14 days	40 MPa	1.5 MPa
Strength at 28 days	43 MPa	2 MPa

A castable extrudable construction material CM1 is prepared in a concrete batching plant (A) typically with help of a mixing vessel (1) with mixing propellers (2) according to the above mix designs described in Tables E and F. The various ingredients of the CM1, as well as possibly ADMS2, ADMS1 and VMA, are stored
5 for instance in the series of silos (3) or dispensers at the batching plant.

The homogenized mixed CM1 that optionally may contain ADMS2 or ADMS1 is transferred from the mixing unit (1, 2) to a concrete truck (CT) that is transporting CM1 to the 3D printing job site.

At the job site, the CM1 is transferred from the concrete truck CT using for
10 instance a concrete pump (4) and a pipe (5) (or any other continuous or discontinuous transportation means) to the 3D printer body (6/8), comprising amongst other a pumping device (9) and a nozzle/die (10). Alternatively, the CM1 is first poured from the concrete truck CT into a hopper or a transition storage (BT) tank or any of the like (not showed) connected to the 3D printer body (6/8) via the
15 pump 4 and the pipe 5 and is transported to the printing device (6,8, 10) equipped with a pump or an infinite screw (9).

Depending which admixture system ADMS2 or ADMS1 is added first, the same first added admixture can be added in CM1 at various steps of the process (e.g., in the ready-mix plant, during transportation, during the storage at the job site,
20 or in the printer head, whereas the second admixture system ADMS2 or ADMS1 can only be added in the printer head to transform CM1 into CM2 and finally CM2S.

An entry (11) (not shown) provided on the extruder/printer head body (6/8), enables the addition of the ADMS1 or ADMS2 to the CM1 to obtain CM2 that is moving towards the die or the nozzle (10), containing both ADMS2 and ADMS1.
25 The construction material CM2, containing both ADMS2 and ADMS1, reacting together to form the 3D network of polymers, is extruded through the nozzle (10). The motor of the printer head (6) and the infinite screw (9) are selected so that the CM2 stiffened (CM2S) can be extruded through the printing nozzle (10). In another particular embodiment, the printer had (6) may include inside the body (8) a mixer
30 or a set of mixing blades (not shown), located uphill from the infinite screw (9).

The resulting stiffened constitution material (CM2S), exiting the nozzle or the die (10) is sufficiently resistant to support its own weight without dimensional changes, for instance to form a part of or a continuous deposition layer on previously

printed/deposited layers. The claimed dosages of ADMS2 and ADMS1 enable to obtained yield shear values between 20 and 50 KPa for the various concrete mix designs that were used for 3D printing tests. These values are over one order of magnitude higher than those obtained in EP3260258B1 using rheological modifying agents in mortars, demonstrating that the stiffness of CM2 (and CM2S) is much higher thanks to the present invention, enabling, amongst others, to use larger sized aggregates that remain stable in CM2S with no risk of segregation.

Finally, successful application of the invention was done using non cementitious binders (e.g. geopolymers) obtained using slag, ground granulated furnace slag, natural pozzolans, mechanically activated glass residues or aluminosilicates industrial by-products, fly ashes or any combination thereof. With respect to the current invention, the process requires to add a chemical activator to CM1 or to ADMS2 (e.g. soluble silicates, colloidal silicates, Na(OH) or Ca(OH)₂, etc.) and the exact types of chemicals for ADMS2 and ADMS1 are dependent on the type of binders and are not disclosed in this application.

Discussion of the results

Although the invention is not limited to the examples provided in the tables E and F, as we can easily understand that the binder content range (cement and/or pozzolans) or the aggregates' content can be extended or modified within the claimed ranges.

Table E shows that all concrete mix designs and dosages of ADMS2, PCE and ADMS1 located within the claimed respective ranges can be transported as fluid concrete until they are stiffened close to the extrusion nozzle to enable the deposition of the construction material CM2S that will maintain its shape once extruded and enable additional layers of CM2S to be added without collapsing under the weight of the additional layers.

The sequence of addition of in which ADMS1, ADMS2 and ADMS3 and WRA in CM1, prior to obtaining CM2 does not influence the final rheological properties of CM2 or the mechanical resistance obtained after hardening.

Amongst others, the method according to the invention presents a large scope of advantages that have no equivalent in the prior art:

- The method according to the invention enables to print construction materials that are true concrete, with aggregates sizes up to 16 mm /actually limited by the dimensions of the printing nozzle as other tests have shown that aggregates up to 32 mm can be used with no effect on the properties of CM2S.
- 5 - The method according to the invention avoid having silos (cement, mineral additions, fine and coarse aggregates, water, admixtures, etc.) for mixing the components of the construction material to be printed on the job site, avoiding thus important manpower, time consuming refilling steps, etc.
- The method according to the invention maintains all the advantages of
10 construction materials mixed in an industrial concrete mixing plant, in terms of mixing efficiency, quality, reliability and constant quality of the delivered construction material.
- Furthermore, the process according to the invention enables to print important quantities of construction material per hour) depending though on
15 the dimensions of the printing nozzle) reaching up to 6 m³/hour that is unparalleled in the industry today. This capability is related to the very fast interaction between ADMS2 and ADMS1, and to the fact that the process does not rely on hardening/setting accelerators or rheology modifiers, that have limited effect even when used in combination.
- 20 - The process according to the invention is also very flexible, versatile and robust compared to the solutions proposed in the prior art as the additions of CMS1, CMS2 and optionally CMS3 and WRA can be adapted to the specifics of the industrial and jobsite contexts.

The method according to the invention presents also the advantages to avoid
25 the need of a dedicated mixer mounted on the printer head (6,8) in combination with the conveying injection device 9. Such an additional mixer mounted on the printer head is typically required when set accelerators are used or if the ingredients of the material to be printed are mixed or remixed close to the printing nozzle.

The method according to the invention can be used for any shape that can be
30 3D printed (walls, containers, vessels, profiles, pillars, slabs, hollow shapes, with a wall thickness ranging from 0,01 m to 1.5 meters (mono-wall or multiple parallel walls).

The method according to the invention can also be used for extruded construction materials to produce profiles, tubes, rails, etc. at industrial scale, by replacing the 3D printing nozzle by an extrusion dies.

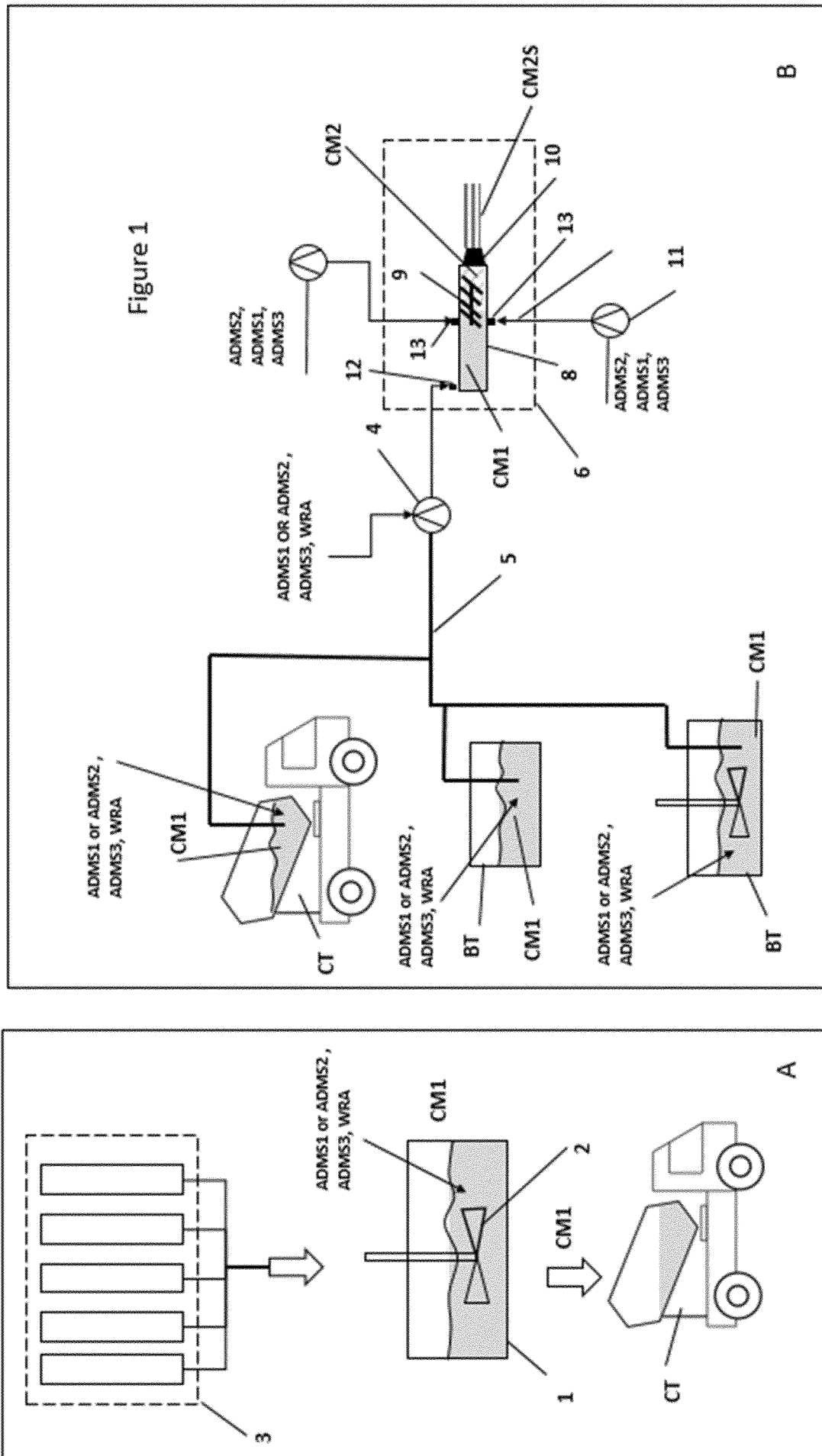
CLAIMS

1. 3D printing industrial production method for fresh construction material containing a hydraulic binder, said method comprising the following steps:
- 5 h) Preparing a ready-mix construction material (CM1) in a concrete-type mixer or concrete batching plant or local static concrete mixer or concrete truck, from the following mix design:
- Binder (250 to 700 kg/m³);
 - Water (100 to 455 kg/m³);
 - 10 - Sand (400 to 1100 kg/m³);
 - Aggregates having a size from 4-16 mm, preferably from 4-12 mm, (400 to 1200 kg/m³);
- i) Transporting CM1 obtained in a) from the concrete-type mixer or concrete batching plant or local static concrete mixer or concrete truck, to a
- 15 jobsite equipped with a 3D printing equipment;
- j) Optionally transferring CM1 into a buffer container at the jobsite;
- k) Moving the CM1 towards a printer head of the 3D printing equipment;
- l) Adding a first (ADMS1) and/or second (ADMS2) admixture system to CM1, uphill from a nozzle of the printer head of the printing equipment yet at a
- 20 distance located from 0.2 m to 4 m from the nozzle, to obtain a second construction material (CM2), provided that:
- ADSM1 is added in step e) when ADMS2 is added in step a), b), c) and/or d);
- ADSM2 is added in step e) when ADMS1 is added in step a), b), c) and/or d); or
- ADMS1 and ADMS2 are both added in step e); and
- 25 wherein ADMS1 comprises at least a high molecular weight, non-ionic water-soluble component, and is dosed at a range from 0.0001 to 0.5 weight% of the binder content;
- wherein ADMS2 comprises at least a polymerized system containing a conjugated or aromatic/non-aromatic, homocyclic/heterocyclic, mono-ring, bi-ring or poly-ring
- 30 system that contains solubilizing functional groups, and is dosed at a range from 0.05 to 5 weight% of the binder content;
- m) Extruding CM2 obtained in e) through the nozzle of the printed head of the printing equipment;

n) Recovering the stiffened construction material (CM2S) after the nozzle of the printed head of the printing equipment.

2. 3D printing industrial production method according to claim 1, wherein (i) a
5 third admixture system (ADMS3) is added to CM1 in step a), b), c), d) and/or e);
and/or (ii) a water reducing agent (WRA) is added in step a), b), c) and/or d); and
wherein ADMS3 comprises further components chosen from the group consisting
of setting or hardening accelerators, pigments, air entrainers, anti-freezing agents,
retarders, and any mix thereof, and is dosed at a range from 0.1 to 3.5% weight%
10 of the binder content.
3. 3D printing industrial production method according to claim 1 or 2, wherein
CM1 further comprise mineral and/or metallic fibers.
- 15 4. 3D printing industrial production method according to any of claims 1 to 3,
wherein the binder is a cement selected from ordinary Portland cement.
5. 3D printing industrial production method according to any of claims 1 to 4,
wherein ADMS1 is selected from polyethylene glycol, polyethylene oxide,
20 polyamine, or a mixture thereof.
6. 3D printing industrial production method according to any of claims 1 to 5,
wherein ADMS2 is selected from the group consisting of benzene, triazine,
naphthalene, anthracene, pyrene, phenanthrene, isoquinoline, and chrysene,
25 containing solubilizing functional groups such as sulfate, carboxylic acid, nitrate.
7. 3D printing industrial production method according to any of claims 1 to 6,
wherein ADMS2 is dosed to the CM2S in range from 0.05 to 5 weight% of the binder
content.
30
8. 3D printing industrial production method according to according to any of
claims 1 to 7, wherein the ratio between ADMS1 and ADMS2 ranges from 1/2000
to 1/200 in the CM2 or CM2S construction material.

9. Use of a CM2S obtained by a method according to any of claims 1 to 8, to continuously produce rails, plates, barriers, rods, bars, hollow pipes, roof tiles or the same; or to deposit by 3D printing successive layers to form walls, piles, pillars or
- 5 the same.



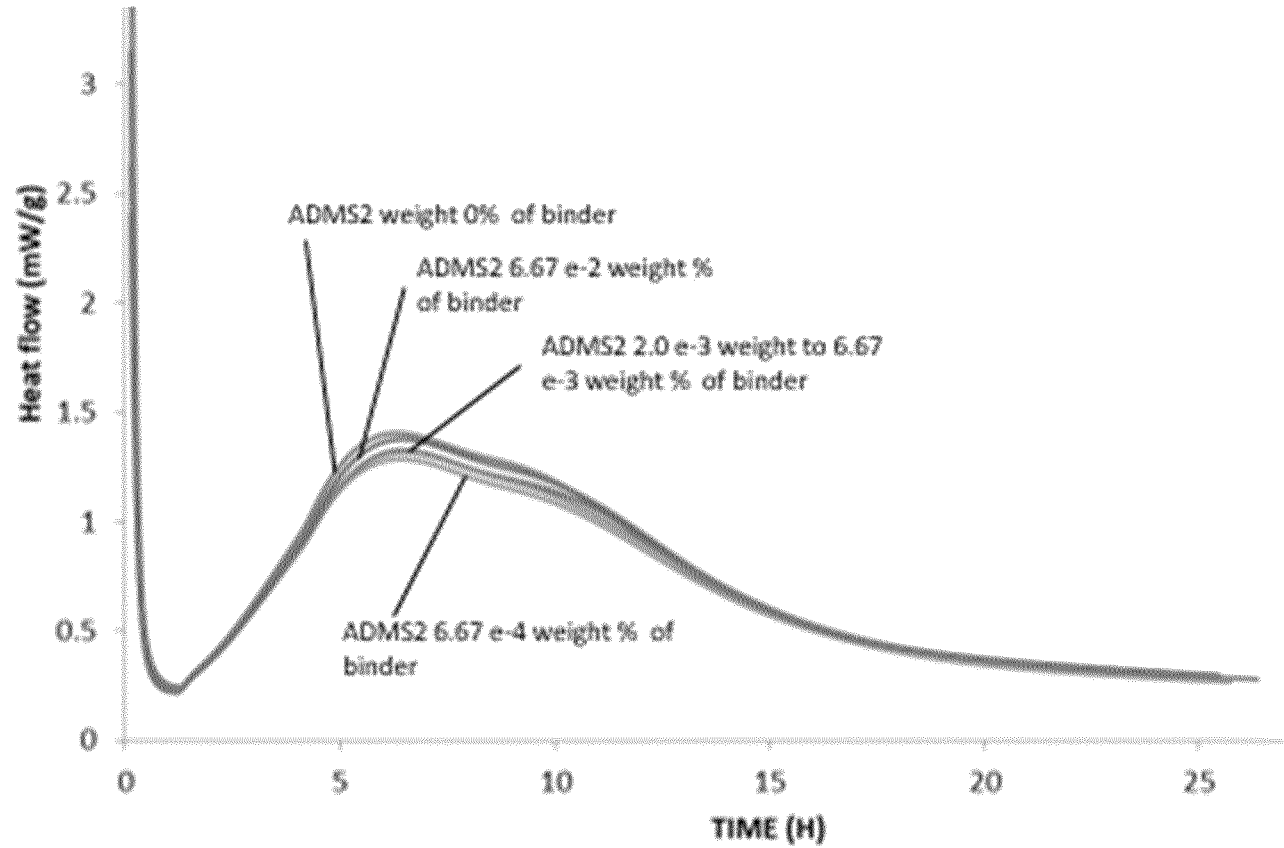


FIGURE 2

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2024/051535

A. CLASSIFICATION OF SUBJECT MATTER					
INV.	B28B1/00 C04B24/20	B01F33/00 C04B24/26	B28C7/04 C04B24/32	B28C7/16 C04B28/04	B28C9/00 B33Y10/00
ADD.					
According to International Patent Classification (IPC) or to both national classification and IPC					
B. FIELDS SEARCHED					
Minimum documentation searched (classification system followed by classification symbols)					
B28B B01F B28C C04B B33Y					
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched					
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)					
EPO-Internal, WPI Data					
C. DOCUMENTS CONSIDERED TO BE RELEVANT					
Category*	Citation of document, with indication, where appropriate, of the relevant passages		Relevant to claim No.		
A	US 2022/250986 A1 (FEICHTENSCHLAGER BERNHARD [DE] ET AL) 11 August 2022 (2022-08-11) paragraphs [0007], [0018], [0114], [0181], [0208] - [0211], [0236] - [0238], [0243] - [0246] -----		1 - 9		
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☒ Further documents are listed in the continuation of Box C.			☒ See patent family annex.		
* Special categories of cited documents :					
"A" document defining the general state of the art which is not considered to be of particular relevance			"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention		
"E" earlier application or patent but published on or after the international filing date			"X" document of particular relevance;; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone		
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"O" document referring to an oral disclosure, use, exhibition or other means			"&" document member of the same patent family		
"P" document published prior to the international filing date but later than the priority date claimed					
Date of the actual completion of the international search		Date of mailing of the international search report			
23 May 2024		12/06/2024			
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Voltz, Eric			

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2024/051535

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2024/051535

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