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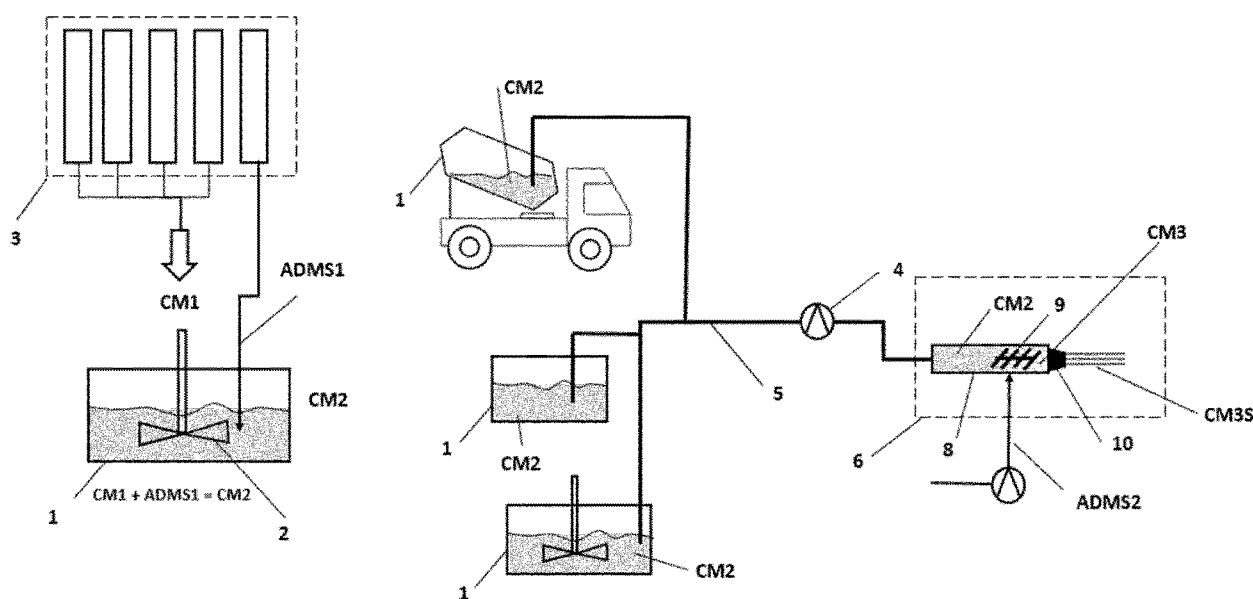


FIGURE 1

(57) Abstract: The present invention relates to a new formless production process to enable to place a construction material (CM3) by extrusion or 3D printing in a continuous or semi continuous manner.

FORMLESS PRODUCTION PROCESS TO PLACE A CONSTRUCTION MATERIAL IN A CONTINUOUS MANNER

DESCRIPTION

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Technical field of the invention

The present invention relates to a new formless production process to enable to place a construction material by extrusion or 3D printing in a continuous or semi continuous manner.

10

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 job sites, or in precast operations. The concrete is then maintained in the form until some level of strength is achieved
15 (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, or reduction of manipulation costs are driving a shift in the way construction materials
20 (e.g., concrete or similar) are placed on jobsite. 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 of the concrete rheology at different moment of the production chain (mixing the concrete, transporting the
25 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 rapidly develop strength.

The production rate, expressed as linear meters of extruded concrete placed by
30 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.

US 5123831 for instance describes a concrete extrusion device for concrete 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.

- 5 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
10 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 or the stiffening of the concrete.

- 15 EP3421201B1 describes a cementitious and mortar formulation for extrusion or 3D printing containing mineral fillers and slag additions on top of the conventional concrete or mortars 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
20 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 during the extrusion/3D printing process.

WO2011066192A1 also describes a mortar or concrete formulation for extrusion,
25 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, superplasticizers, water binding agents, viscosity modifiers, corrosion inhibitors, pigments, wetting agents, water soluble polymers, etc.). As previously, the composition of the concrete and the
30 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 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.

5 Finally, 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 polyacrylamide, casein, and/or Welan gum. The patent only provides examples of mix
10 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 ® premix) 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
15 drawbacks as the stiffness of the mortars that can be obtained leaving the nozzle is limited.

As a conclusion, the prior art does not disclose any production process that describes the use of a large variety of mortar or concrete mix designs, containing optionally metallic fibers or suing aggregates larger than 2 mm. Furthermore, the prior
20 art does not disclose a robust technology to radically transform a fluid concrete with a low water/binder ratio, to a very stiff concrete once leaving the printing nozzle or the extrusion die.

Description of the invention

25 The objective of the present invention is to provide an overall production process to place a wide range construction materials of any shape, hollow or not, with hardened resistance (compression according to EN 12390-3 or RILEM document) ranging from 1 MPa to 150 MPa, with materials densities ranging from 300 Kg/m³ to 2'400 Kg/m³, with or without fibers reinforcement (for instance steel fibers from 15 Kg/m³ to 100
30 Kg/m³ or any other types of fibers) without using frames or forms, using extrusion or 3D printing and ensuring a high production rate while providing for a radical change of the rheological properties of the fluid/plastic construction material between the state prior to the extrusion die or nozzle and the material exiting the die/nozzle.

The invention therefore consists of or comprises a formless production process for fresh construction material to enable to place said construction material by extrusion or 3D printing in a continuous or semi continuous manner, as described in Figure 1.

- 5 An object of the present invention is therefore a formless production process for fresh construction material containing hydraulic binder comprising or consisting of the following steps :

A- Preparing a second construction material (CM2) from the following mix design of a first construction material (CM1) in a concrete-type mixer or concrete
10 batching plant or local static concrete mixer or concrete truck:

- Binder (100 to 800 kg/m³ of CM1);
- Water (50 to 350 Kg/m³ of CM1);
- Sand (10 to 1500 Kg/m³ of CM1);
- Aggregates having a size from 4-16mm, preferably from 4-12 mm (0 to

15 1500 Kg/m³ of CM1); and

an admixture system (ADMS1) which is added to CM1 to obtain the second construction material (CM2),

wherein ADMS1 comprises at least a high molecular weight, non-ionic water soluble component (ADMS1-CA), and is dosed at a range between 0.001 weight % and 2

20 weight % of binder content.

B- Transporting CM2 obtained in A- from the concrete-type mixer or concrete batching plant or local static concrete mixer or concrete truck to an extruding device, while adding a second admixture system (ADMS2) to CM2 to obtain a third construction material (CM3) that is moving inside the extrusion device towards the
25 nozzle/die, uphill from the extrusion nozzle or die of the extruding device yet at a distance is located between 0.2 m and 4.0 m from the extrusion nozzle or die, wherein ADMS2 comprises at least a polymerized system containing a conjugated or aromatic, bi- or poly-ring system that contains solubilizing functional groups (ADMS2-CA), and is dosed at a range of 0.01% to 5% of the binder content;

30 C- Extruding CM3 obtained in B- through the extrusion nozzle or die.

D- Recovering the stiffened construction material (CM3S) after the nozzle or printer head, that enable the extruded form to keep its shape or the printed layer to support its own weight without dimensional changes.

Said stiffened construction material CM3S can thus be submitted to conventional hardening/curing (between 5°C to 50°C and with an air moisture between 10% to 95%) by means well known to the skilled person, to achieve its final strength.

According to a particular embodiment of the present invention, the first construction material (CM1) is a dry mix of binder, sand, and aggregates to which water is then added. All said components are mixed in the concrete-type mixer to produce the first construction material (CM1) to which the first admixture system ADMS1 containing optionally accelerators is further added to obtain the second construction material (CM2).

10 According to a particular embodiment of the present invention, the binder material is selected from ordinary Portland cement (CEM, CEM II CEM III CEM IV), or cement-free binder containing slag, fly ash, natural pozzolans, activated clay, limestone, glass or any other aluminosilicate, or any combination thereof (e.g. see International Application WO2017122916).

15 According to a particular embodiment of the present invention, the high molecular weight, non-ionic water soluble component (ADMS1-CA) is selected from polyethylene glycol (PEG) or polyethylene oxide (PEO), polyamine, or a mixture thereof. For example, the polyethylene glycol 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 1 weight % of binder content. 20 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 0.001 weight % and 2 weight % of binder content.

According to a particular embodiment of the present invention, the admixture system ADMS1 may further comprise at least one strong PCE based water reduction admixture (ADMS1-CB), to allow for low water/binder contents and high strength hardened construction, while maintaining good fluidity and pumpability. 25

According to a particular embodiment of the present invention, the ratio between ADMS1-CB and ADMS1-CA in ADMS1 expressed in dry solid content weight is located 30 between 0 and 1000.

According to a particular embodiment of the present invention, the construction material CM1 or CM2 may further comprise at least one component among: foam, lightweight aggregates, organic, mineral and/or 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, etc.

According to a particular embodiment of the present invention, the ADMS2-CA reactant comprising at least a polymerized system that can be chemistry containing conjugated
5 or aromatic, bi-ring or polyring system ADMS2-CA (polyring equal two or more rings of any size) that contains solubilizing functional groups selected from naphthalene, anthracene, pyrene, phenanthrene, isoquinoline, chrysene.

According to a particular embodiment of the present invention, the second admixture system (ADMS2) may contain further components like setting or hardening
10 accelerators (e.g. calcium nitrate, calcium formate, calcium chloride).

According to a particular embodiment of the present invention, the first admixture system ADMS1 is dosed so that the slump of the construction material CM2 is located between S3 and S5 according to EN 206, or the slump flow between SF1 and SF3 according to EN 206, or between 200mm and 700mm according to EN 12350-8.

15 According to a particular embodiment of the present invention, the second admixture system ADMS2 is dosed to the second construction material CM1 containing ADMS1 (CM2) in range of 0.01% to 5% of the binder content so that the ratio ADMS1-CB to ADMS1-CA in ADM1S expressed in dry solid weight % of binder content is located between 0 and 1000 and the ratio between the ADMS1-CA in
20 ADMS1 and the polymerized system ADMS2-CA in ADMS2 expressed in dry solid weight % of binder content is located between 0.001 and 1, to trigger a strong interaction between ADMS1 and ADMS2 so that the reaction provides the highest possible material stiffness to CM3S. The dosage of ADMS2-CA in ADMS2 allows to adjust the stiffening of CM1 depending on requirements and operating conditions.

25 Another object of the present invention is therefore the use of CM3S 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 the same.

The important increase of the yield shear vane value, or ability to maintain shape
30 after extrusion of the construction material after adding ADMS2 is due to a chemical strong interaction between ADMS1 and ADMS2. The reaction in the form a polymerization produces a 3D connected net that immediately reduces the fluidity of the construction by an 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

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 and thus formation of a supramolecular network which gives the increased in the yield stress and thus results in the observed stiffening reaction.

The main reason why component ADMS2-CA (e.g. naphthalene) is added in step C- and the ADMS1-CA is added in step B-, is related to the option to strongly modify the rheology of CM1 using ASDMS1-CB. ADMS2-CA alone cannot provide efficient water reduction in CM1, and adding ADMS1-CA together with ADMS2-CA, result in a strong interaction between the 2 components that would very negatively affect the requested fluidity of CM2 that would difficult pumpable.

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, GGBS, fly ash, microsilica limestone filler
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 use 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 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	Manufactured, natural or recycled minerals with a particle size typically greater than 0-4 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-chain such as EO and/or PO. 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 25Mpa
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, fly ash, slag, silica fume, etc.)
w/b	Total free water (w) mass in Kg divided by the total binder mass in Kg
Workability	The workability of a material is measure with a slump test (table 1: slump)
CM1	Construction material according to the invention at step A
CM2	Construction material according to the invention at step B, after adding ADMS1
CM3	Construction material according to the invention at step D, after adding ADSM2 to CM2, that is moving towards the nozzle or die of the extruding device
CM3S	Stiffened construction material according to the invention recovered at step E, after extrusion through the nozzle or die

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
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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

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

Figure 1 is a schematic representation of the invention device that can be used to carry out the claimed invention, presented to better understand the invention.

EXAMPLES

EXAMPLE 1: IMPLEMENTATION OF THE CLAIMED FORMLESS PRODUCTION PROCESS FOR FRESH CONSTRUCTION MATERIAL

The mixes described in tables 1 and 2 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 figure 1.

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 150kg/m³ to 1000kg/m³.

The metallic fibers are characterized by a ratio length to diameter ranking from 20 to 120, with a total length located between 10mm to 100mm. The metallic fibers are

straight or hooked fibers with tensile strength located between 600MPa and 4000MPa and E Modulus located between 185GPa and 215GPa

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

- 5 Extrusion dies have opening sizes ranking from 0.04 m² to 1 m², preferably to 0.6 m².

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 shapes.

- 10 Admixture ADMS1 ranges are limited for low dosage to the minimum level of consistency required (min=S3 or SF1); passing the upper dosage limit will generate a risk of segregation of the aggregates as the construction material will be too fluid.

The consistency properties were measured according to the details provided in Table 1.

- 15 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 cubes in compression according to norm EN 12390-3.

Table 1: Examples of mix designs and properties using dense silicates/limestones aggregates and sand

	MD 1	MD2	MD3	MD4	MD5	MD6
Main Binder type	Cement	Cement	Cement	Cement	Cement	Cement
Main binder Dosage kg/m3	450	450	370	450	450	450
Second Binder type	NA	Microsilica	Limestone filler	NA	NA	NA
Second binder dosage (kg/m3)	NA	45	130	NA	NA	NA
Water kg/m3	200	160	190	280	200	280
Sand kg/m3	798	908	804	693	798	693
Large aggregates size	4-10 mm crushed	4-8mm round	4-12mm round	4-8mm round	4-8mm round	4-8mm round
Large aggregates kg/m3	877.8	817	804	763	878	762
Metallic fibers	NA	NA	40kg/m3	NA	NA	NA

Set	In usual dosage, 0-5.00% of total binder content	0	In usual dosage, 0-5.00% of total binder content	0	In usual dosage, 0-5.00% of total binder content	0
ADMS1 component ADMS1-CB	PCE	PCE	PCE	NA	PCE	NA
ADMS1 component ADMS1-CA	PEO/PEG	PEO/PEG	PEO/PEG	PEO/PEG	PEO/PEG	PEO/PEG
ADMS1-CB dosage as a percentage of total binder	0.084%(0.38kg/m ³)	0.35% (1.72kg/m ³)	0.09% (0.45kg/m ³)	NA	0.084% (0.38kg/m ³)	NA
ADMS1-CA component dosage vs binder content	0.0042% (0.0189 kg/m ³)	0.0058% (0.029kg/m ³)	0.0043% (0.01075kg/m ³)	0.0042% (0.0189 kg/m ³)	0.0014% (0.0063kg/m ³)	0.0010% (0.0045kg/m ³)
Consistency with ADMS1 (step B) in CM1	slump flow between 300-550mm	slump flow between 300-550mm	slump flow between 300-550mm	slump flow between 300-550mm	slump flow between 300-550mm	slump flow between 300-550mm
ADMS2-CA	NPS	NPS	NPS	NPS	NPS	NPS

ADMS2-CA dosage of total binder content	0.16%	0.12%	0.16%	0.16%	0.16%	0.16%
Consistency after ADMS2-CA (step F)	Extrudable, no slump concrete	Extrudable, no slump concrete	Extrudable, no slump concrete	Extrudable, no slump concrete	Non extrudable	Non extrudable
Shear vane value (KPa)	30	28	42	38	8	10
Strength at 1 day (on cubes)	20MPa	40.3MPa	18MPa	8MPa	20.0MPa	8MPa
Strength at 7 days (on cubes)	46.8MPa	80.5MPa	35.8MPa	13MPa	46.8MPa	13MPa
Strength at 14 days (on cubes)	50MPa	85MPa	40MPa	18MPa	50.0MPa	18MPa
Strength at 28 days (on cubes)	53.9MPa	90MPa	45MPa	22MPa	53.9MPa	22MPa

Components of the first admixture system ADMS1 are selected from PEO/PEG, and eventually plasticizers, superplasticizers, which provide excellent consistency values even for CM1 mixes with very low water/binder ratio (lower than 0,45), so the final strength of the hardened and cured final material as can be seen in the Table 1 for different mix designs presented. The consistency obtained on step B- presents the advantage to enable a construction material that is easily pumpable, this reducing the efforts and the energy consumption of the transportation of step C-. Furthermore, the consistency at step B- can be chosen without considering the final low consistency (or high stiffness) of the final extruded/3D printed material, as would be the case if all required ingredients would be present in a unique mix design with constant rheological properties throughout the whole process.

It can be seen in table 1 that if the dosage of ADMS1-CA is too low, the consistency change is not high enough and the shear vane value is low. Concrete shows a slump value and the required stiffness cannot be obtained (not extrudable). If ADMS2-CA is below specified dosage, the consistency change is not high or efficient enough and the concrete is too soft and too fluid to be extrudable. If ADMS2-CA is above specified dosage, the consistency change will be too important and the concrete consistency will be too dry or stiff to be extrudable through the die or nozzle and could create a blockage. If ADMS1-CB is too low, the water reduction effect is too limited, and a high strength concrete cannot be achieved because it is not possible to lower the water/binder ratio sufficiently. If ADMS1-CB is too high, the concrete might be segregated due to a very strong water-reduction effect leading to pumpability and extrusion failures.

Table 2: Examples of mix designs and properties using light weight aggregates and air entrainer

	MD 1	MD2
Main Binder type	Cement	Cement
Main binder Dosage kg/m3	360	250
Second binder type	Fly ash	NA
Second binder dosage kg/m3	200	NA
Water kg/m3	170	138
Lightweight Sand kg/m3	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
Air measured	NA	50%
Metallic fibers	NA	
ADMS1 component ADMS1-CB	PCE	PCE
ADMS1 component ADMS1-CA	PEO/PEG	PEO/PEG
ADMS1 component ADMS1-CB dosage as a percentage of total binder	0.33% or 1.85kg/m ³	0.1% or 0.24kg/m ³
ADMS1 component ADMS1-CA dosage as a percentage of total binder	0.0055% or 0.031kg/m ³	0.0016% or 0.004kg/m ³
Consistency with ADMS1 (step B) in CM1	S4-S5	S4-S5
Other Consistency with ADMS1 (step B) in CM1	SF1 to SF3	SF1 to SF3
ADMS2-CA type	NPS	NPS
ADMS2-CA dosage as percentage of total binder	0.16% (0.9kg/m ³)	0.16% (0.40kg/m ³)
Consistency after ADM2 (step F)	extrudable	extrudable
Other consistency with ADMS2-CA (step F)	S1 to S2	S1 to S2
Strength at 1 days	21MPa	0.5MPa
Strength at 7 days	36MPa	1MPa
Strength at 14 days	40MPa	1.5MPa
Strength at 28 days	43MPa	2MPa

It could be demonstrated that using ADMS1-CB in ADMS1 does not impact the stiffness resulting in CM3 when using the dosages claimed for the different components.

- 5 The implementation of the process of the present invention is not limited by the schema presented in figure 1. A castable extrudable construction material CM2 is

prepared in a concrete-type mixer or concrete batching plant or local static concrete mixer or concrete truck (1) typically with help of mixing propellers (2). The various ingredients of the CM1, as well as ADMS1, are stored for instance in the series of silos (3) or dispensers. The homogenized mixed CM1 containing the ADMS1 (CM2) is transferred from the concrete-type mixer or concrete batching plant or local static concrete mixer or concrete truck (1), using for instance a pump (4) and a pipe (5) (or any other continuous or discontinuous transportation means) to the extruder/3D printer body (6/8), comprising amongst other a pumping device (9) and a nozzle/die (10). For instance, the CM1 containing the ADMS1 (CM2) is poured into a hopper, a transition storage tank or any of the like (not showed) connected to the extruder/3D printer body (6/8) or directly injected, and is transported to the printing/extruding nozzle/die (10) using a pump or an infinite screw (9). An entry (11) (not shown) provided on the extruder/printer head body (6/8), enables the addition of the ADMS2 to the CM1 containing the ADMS1 (CM2) to obtain CM3 that is moving towards the die or the nozzle (10), containing both ADMS1 and ADMS2. In a preferred embodiment, the ADMS2 is added into the pump or screw (9), using a piping system, a pump, a dosing system and a ADMS2 silo (not showed on figure1). The construction material CM3, containing both ADMS1 and ADMS2, reacting together to form the 3D network of polymers, is extruded, pressed through the nozzle of the die (10). The resulting stiffened constitution material (CM3S), 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.

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 alumino silicates 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 ADMS1 (e.g. soluble silicates, colloidal silicates, Na(OH) or Ca(OH)₂, etc.) and the exact types of chemicals for ADMS1-CA and ADMS2-CA are dependent on the type of binders and are not disclosed in this application.

Advantages

Typically, the invention enables to continuously extrude shapes like rails, plates, barriers, rods, bars, hollow pipes, roof tiles or the same; and enables a printer to deposit successive layers of CM3S to form walls, piles, pillars or the same.

The use of metallic fibers advantageously replaces steel rebars that are impossible to place in a normal extrusion or 3D printing Process.

This drawback of the technology according to the prior art is solved by the present invention.

The advantages resulting from the invention are multiple:

- 10 • It provides with a very versatile process that enables to use almost any type of binder, for applications like extrusion of parts (rods, profiles, rails, tubes) or layer by layer 3D printing.
- 15 • It provides with a solution to control the rheology of the construction material at fresh state along the whole manufacturing steps A to H so the fluidity of the construction material can be adapted throughout the process to minimize transporting issues, wear or requiring the use of high costs high maintenance demanding equipment.
- 20 • It provides with a solution to control the final hardened strength of the extruded construction material by adjusting dosages of components in the 2 admixture systems, without have form instance to use ultra-high-strength cements to achieve high resistances as in EP3260258.
- 25 • It provides with solution to extrude/3D-print a construction material that contains large aggregates (4-16 mm in size) and is not limited to the use of sand as in the prior art.
- It provided with a solution that enables to use light weight aggregates for instance to improve the thermal insulation of the final product.
- It provides with a solution to use high dosages of reinforcement fibers.

CLAIMS

1) Formless production process for fresh construction material containing hydraulic binder comprising or consisting of the following steps :

5 A- Preparing a second construction material (CM2) from the following mix design of a first construction material (CM1) in a concrete-type mixer or concrete batching plant or local static concrete mixer or concrete truck:

- Binder (100 to 800 kg/m³ of CM1);
- Water (50 to 350 Kg/m³ of CM1);
- 10 - Sand (10 to 1500 Kg/m³ of CM1);
- Aggregates having a size from 4-16mm, preferably from 4-12 mm (0 to 1500 Kg/m³ of CM1); and

an admixture system (ADMS1) which is added to CM1 to obtain the second construction material (CM2),

15 wherein ADMS1 comprises at least a high molecular weight, non-ionic water soluble component (ADMS1-CA), and is dosed at a range between 0.001 weight % and 2 weight % of binder content.

B- Transporting CM2 obtained in A- from the concrete-type mixer or concrete batching plant or local static concrete mixer or concrete truck to an extruding device,
20 while adding a second admixture system (ADMS2) to CM2 to obtain a third construction material (CM3) that is moving inside the extrusion device towards the nozzle/die, uphill from the extrusion nozzle or die of the extruding device yet at a distance is located between 0.2 m and 4.0 m from the extrusion nozzle or die, wherein ADMS2 comprises at least a polymerized system containing a conjugated or
25 aromatic, bi- or poly-ring system that contains solubilizing functional groups (ADMS2-CA), and is dosed at a range of 0.01% to 5% of the binder content.

C- Extruding CM3 obtained in B- through the extrusion nozzle or die.

D- Recovering the stiffened construction material (CM3S) after the nozzle or printer head.

30

2) Formless production process according to claim 1, wherein mineral and/or metallic fibers are added to CM1 or CM2.

- 3) Formless production process according to claim 1 or 2, wherein the binder is selected from ordinary Portland cement.
- 4) Formless production process according to any of claims 1 to 3, wherein ADMS1-
5 CA is selected from polyethylene glycol, polyethylene oxide, polyamine, or a mixture thereof.
- 5) Formless production process according to any of claims 1 to 4, wherein ADMS1-CA is comprised between 0.001 weight % and 2 weight % of binder content.
- 10 6) Formless production process according to any of claims 1 to 5, wherein ADMS1 further comprises at least one strong PCE based water reduction admixture (ADMS1-CB).
- 15 7) Formless production process according to any of claims 1 to 6, wherein the ratio between ADMS1-CB and ADMS1-CA expressed in dry solid content weight is located between 0 and 1000.
- 8) Formless production process according to any of claims 1 to 7, wherein ADMS2-
20 CA is selected from chemicals that contain solubilizing functional groups selected from Naphthalene, anthracene, pyrene, phenanthrene, isoquinoline, chrysene.
- 9) Formless production process according to any of claims 1 to 8, wherein ADMS2 is dosed to the CM2 in range of 0.01% to 5% of the binder content.
- 25 10) Formless production process according to any of claims 1 to 10, wherein CM2 has a slump located between S3 and S5 according to EN 206.
- 11) Use of CM3S obtained by a process according to any of claims 1 to 10, to
30 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 the same.

1/1

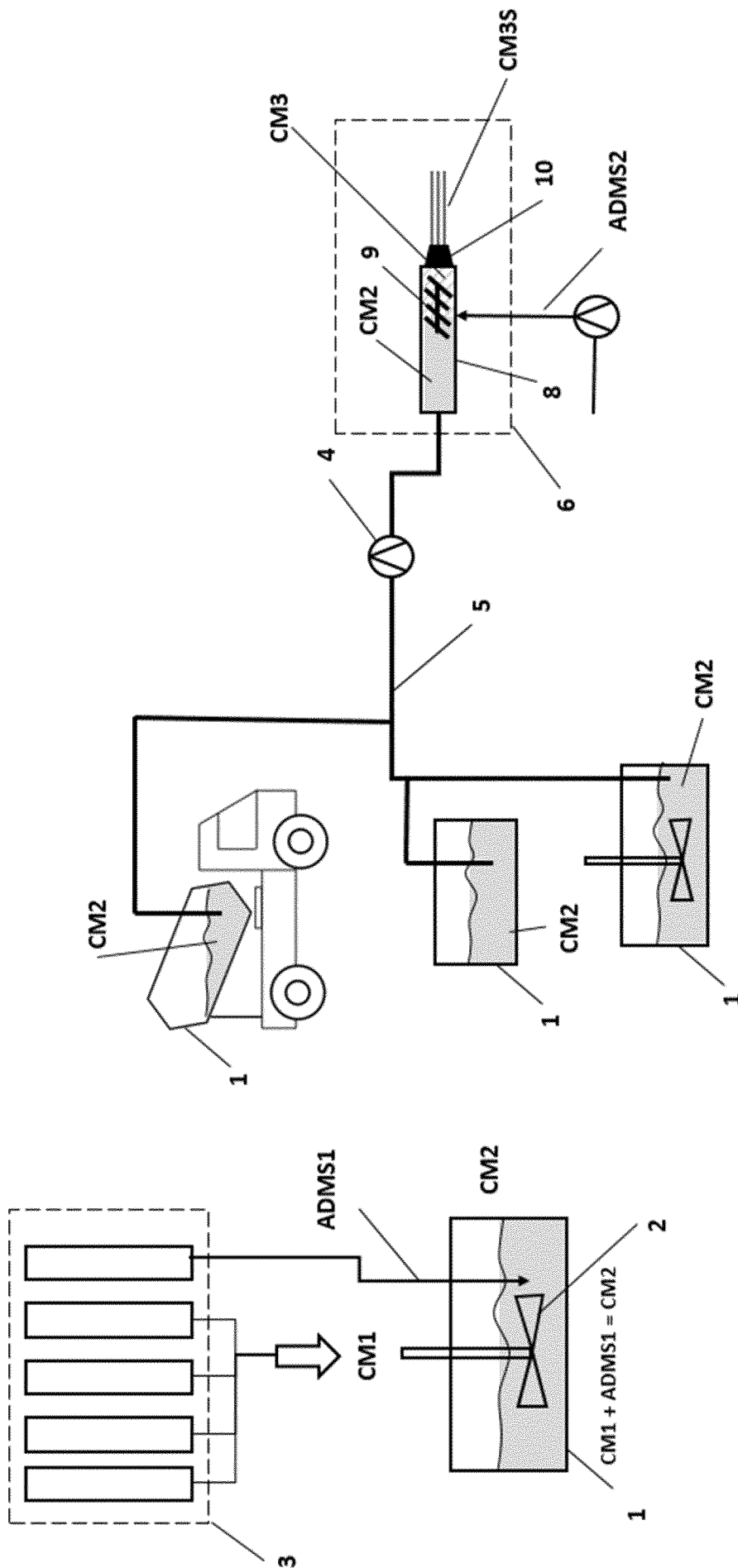


FIGURE 1

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2023/075386

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] -----	1-11
A	US 2019/194072 A1 (ESNAULT VIVIEN [FR] ET AL) 27 June 2019 (2019-06-27) figure 1 paragraphs [0025] - [0034] -----	1-11
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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 "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "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 "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 "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 27 March 2024		Date of mailing of the international search report 12/04/2024
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/EP2023/075386

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Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Information on patent family members

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