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**BENSAID BOULEKBACHE ET AL: "Influence of yield stress and compressive strength on direct shear
behaviour of steel fibre-reinforced concrete", CONSTRUCTION AND BUILDING MATERIALS, ELSEVIER,
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10.1016/J.CONBUILDMAT.2011.07.015 [retrieved on 2011-08-17]**

DESCRIPTION

[0001] The invention refers to a method of placing a flowable construction material comprising a hydraulic binder for building structural components layer-by-layer, such as for 3D concrete or mortar printing.

[0002] US 2015/072068 A1 discloses a method of placing a flowable construction material comprising a hydraulic binder for building structural components layer-by-layer, such as for 3D concrete printing, said method comprising: conveying the flowable construction material to a deposition head and placing the construction material through an outlet of the deposition head in order to form a layer of construction material.

[0003] 3D printing is a building technique that is commonly called "additive manufacturing" and consists of joining material to produce objects, layer upon layer, from 3D model data or other electronic data source. In particular, successive layers of material are formed under computer control by means of an industrial robot. It has already been proposed to develop 3D printers capable of producing structural buildings from a construction material that can be a mortar or a concrete. According to these proposals, the construction material is extruded through a nozzle to build structural components layer-by-layer without the use of formwork or any subsequent vibration. The possibility to build structures without formwork is a major advantage in terms of production rate, architectural freedom and cost reduction.

[0004] Usually, 3D printing of construction materials is a continuous process that comprises conveying fresh concrete or mortar to a deposition head and placing the construction material through an outlet of the deposition head in order to form a layer of concrete. while placing the concrete or the mortar, the deposition head is moved under computer control in order to create a layer of construction material in accordance with the underlying 3D model. In particular, the deposition head places a ribbon of fresh concrete or mortar material. For allowing the fresh concrete or mortar to be moved smoothly through each part of the delivery process to the deposition head, a consistent rheology of the fresh material must be safeguarded.

[0005] However, the construction material must not only be sufficiently fluid for conveying and extrusion purposes, but also sufficiently firm in order to provide the required mechanical stability of the 3D printed structure before the hydraulic binder sets. In particular, the lower layers of the construction material should sustain the load imposed by upper layers without collapsing. The person skilled in the art would therefore tend towards monitoring the material hardening and setting over time. The material must set early enough and harden sufficiently to sustain the weight of the subsequently placed layers. However, hardening of the material typically requires a prolonged time, which does not only result in a prolonged production time, but also in a decrease of the bonding strength between the layers. In order to enhance the bonding strength between the layers, it would be beneficial to place a layer while the preceding layer is still fresh. This in turn has the drawback, that a layer of freshly placed concrete does not have an adequate mechanical strength capable of sustaining the weight of the

subsequently placed layers.

[0006] Therefore, the instant invention aims at improving a 3D printing process of the initially defined kind so as to overcome the above mentioned problems. In particular, the invention aims at providing a specific hydraulic composition and a method that allows a fast construction progress with short time gaps between the placement of successive layers of construction material and that at the same time provides sufficient mechanical strength of the layers capable of sustaining the weight of the subsequently placed layers.

[0007] In order to solve this object, the method according to the invention comprises the features of claim 1.

[0008] Thus, the invention is based on the concept that the ability of the placed layers to sustain its own weight is linked to its rheology and more particularly to its yield stress. During the layer-by-layer building of a structure, the first placed layer undergoes the heaviest load. In order to ensure the structural stability during the process, the yield stress must be sufficient to sustain this load. By adding a rheology-modifying agent to the fluid construction material only shortly before the placement of the material, the construction material retains its ability to flow under relatively low shearing stress in its fresh state to the deposition head, but receives a sufficiently high yield stress when being placed so as to prevent the material from collapsing under its own weight or the weight of the next layers. Therefore, the inventive method combines two seemingly opposite characteristics: the construction material is easy to pump and has an increased yield stress once the material is placed.

[0009] The construction material may be a mortar, i.e. a mixture of a hydraulic binder, potentially additional mineral components such as ground limestone, water, sand, and chemical admixtures.

[0010] The construction material may also be a concrete, i.e. a mixture of a hydraulic binder, potentially additional mineral components such as ground limestone, water, sand, gravel, and chemical admixtures.

[0011] In a preferred embodiment, the construction material is a flowable ultrahigh performance concrete, i.e. a mixture of cement, fine limestone material, micro-sand and/or sand, a high-range water reducing admixture, potentially an accelerating admixture, and water, that develops a compressive strength at 28 days of at least 100 MPa.

[0012] The rheology-modifying agent may be added to the construction material just before reaching the deposition head or in the deposition head.

[0013] Preferably, the rheology-modifying agent and the construction material are mixed with each other before placing the construction material, wherein a static mixer is preferably used for mixing.

[0014] Preferably, the rheology-modifying agent is continuously added to the flow of conveyed construction material so that a continuous process is achieved. Preferably, not only the addition of the rheology-modifying agent, but also the mixing of the rheology-modifying agent with the flow of conveyed construction material is carried out continuously, so that a continuous deposition of the mix of construction material and rheology-modifying agent may be achieved while moving the deposition head in accordance with the underlying 3D data.

[0015] The amount of rheology-modifying agent that is continuously added to the flow of construction material per time unit is preferably controlled in order to adjust a defined ratio of rheology-modifying agent and construction material in the final mixture that is placed layer by layer. In particular, the flow rate of the construction material that is conveyed to the deposition head is measured and the flow rate of the rheology-modifying agent added to the flow of construction material is adjusted to achieve the defined ratio. Alternatively, a fixed flow rate of the construction material conveyed to the deposition head is adjusted and the flow rate of the rheology-modifying agent added to the flow of construction material is selected so as to achieve the defined ratio.

[0016] According to the invention, the step of placing the construction material comprises extruding the construction material in a pasty form through a nozzle of the deposition head.

[0017] The amount of rheology-modifying agent added to the construction material is selected such that a layer of placed material has a sufficient stability in order not to collapse under its own weight or the weight of subsequent layer(s) placed on top. In this connection, a mode of operation consists in that, after the placement of a first layer of construction material, at least one subsequent layer of construction material is placed onto the first layer, wherein the amount of rheology-modifying agent added to the construction material is selected so as to increase the yield stress so that the first layer does not collapse under the load of said at least one subsequent layer.

[0018] In this connection, "not collapsing" means that the height of the layer is not reduced by more than 10%, preferably more than 5%, under the load of the at least one subsequent layer.

[0019] Since the inventive method aims at enabling a fast construction progress, the above stability criteria should preferably be fulfilled at a minimum construction speed as defined by a maximum time gap between the placement of two subsequent layers of material. According to a preferred mode of operation, construction material of the first layer is allowed to rest during a time period of not more than 2 minutes, preferably during a time period of 30-60 sec, before construction material of a subsequent layer is placed onto the said construction material of the first layer.

[0020] According to a preferred embodiment of the invention, the yield stress of the freshly placed construction material is 600 - 4000 Pa. Therefore, it is preferably proceeded such that the amount of rheology-modifying agent added to the construction material is selected so as to increase the yield stress to 600 - 4000 Pa. The yield stress is measured with a scissometer. A

scissometer consists of a vane plunged into the material to be tested and to which an increasing torque is applied. When a failure occurs in the material, the vane starts to rotate, generally as the torque reaches its maximum value, which is considered as the characteristic value that is representative of the yield stress of the material. The yield stress measurement is preferably carried out within 30-60 sec after the material has been placed.

[0021] The addition of a rheology-modifying agent according to the invention results in that the increased yield stress property is attained almost instantly after placement, that is to say before the setting has occurred. Therefore, the increase in yield stress that is achieved by the invention is independent from the setting process of the hydraulic binder of the construction material. Thus, the invention generally does without controlling or accelerating the setting process.

[0022] However, in a preferred embodiment of the invention, even better results may be achieved by additionally accelerating the setting process. This allows to further increase the construction speed. In particular, a setting or hardening accelerator salt, such as, e.g., sodium chloride, calcium chloride, aluminum hydroxide, aluminum-potassium sulfate, sodium silicate, calcium nitrate and/or calcium nitrite, sodium and/or calcium thiocyanate, is preferably added to the hydraulic binder before, during and/or after the conveying step. An accelerating admixture may also be used that function both as setting accelerator and as rheology-modifying agent. Aluminum-potassium sulfate and sodium silicate may be mentioned as examples of admixtures that provide both functions.

[0023] A commercial accelerator typically used for shotcrete applications may also be used, such as Sika 40 AF, or CHRYSO®Jet products, at dosages comprised between 1.0 and 10%, more preferentially between 3.0% and 7% of the total weight of hydraulic binder.

[0024] The rheology-modifying agent may be any admixture that increases the yield stress of the placed material before setting of the hydraulic binder occurs. Preferably, a thickening agent or a viscosity enhancer is used as said rheology-modifying agent. This agent is preferentially used in liquid form. In particular, starch ether, cellulose ether and/or welan gum is used as the rheology-modifying agent or as a component of the rheology-modifying agent. Particularly good results have been achieved with the following admixtures: Foxcrete S200 (starch ether) provided by Avebe, Aquasorb 2611 (water soluble polyacrylamide) provided by SNF Floerger SAS, Tylose MHS 300000 P6 (water soluble, non-ionic, highly etherified methyl hydroxyethyl cellulose) provided by SE Tylose GmbH & Co. KG, KelcoCrete (diutan gum) provided by CP Kelco and casein.

[0025] The conveying step of the inventive method comprises conveying the construction material in a flowable state to the deposition head. In particular, the conveying of the construction material is performed by pumping. Preferably, the material is conveyed in a wet state and is ready to be placed without the need of adding any additional components with the exception of the rheology-modifying agent.

[0026] Preferably the fresh construction material, such as fresh concrete or fresh mortar, is stored in a silo or any other storage container or in a mixer of a ready-mix delivery truck and is conveyed from the storage site directly to the deposition head.

[0027] Preferably, the construction material during the conveying step, i.e. before the addition of the rheology-modifying agent, is designed to be self-levelling. In particular, the yield stress of the material to be conveyed is between 200 to 400 Pa when measured with a scissometer.

[0028] In order to achieve the conveyability or pumpability described above, a water reducer, in particular a plasticizer or a super-plasticizer, preferably a plasticizer based on polyoxy polycarboxylate or phosphonates, is preferably added to the construction material before the conveying step.

[0029] A water reducer makes it possible to reduce the amount of mixing water for a given workability by typically 10-15%. By way of example of water reducers, mention may be made of lignosulphonates, hydroxycarboxylic acids, carbohydrates, and other specific organic compounds, for example glycerol, polyvinyl alcohol, sodium alumino-methyl-siliconate and sulfanilic acid as described in the Concrete Admixtures Handbook, Properties Science and Technology, V.S. Ramachandran, Noyes Publications, 1984.

[0030] Super-plasticisers belong to a new class of water reducers and are capable of reducing water contents of mixing water, for a given workability, by approximately 30% by mass. By way of example of a super-plasticiser, the PCP super-plasticisers may be noted. The term "PCP" or "polyoxy polycarboxylate" is to be understood according to the present invention as a copolymer of acrylic acids or methacrylic acids and their esters of polyoxy ethylene (POE) .

[0031] Good results have been achieved with the following types of superplasticizers: CHRYSO®Premia, a PCP based high range water reducer, BASF MasterGlenium 27, a PCP based high range water reducer, and CHRYSO®Optima 100, a phosphonate based high range water reducer.

[0032] Preferably, the construction material comprises 0.05 to 1%, more preferably 0.05 to 0.5% of a water reducer, a plasticiser or a super-plasticiser, percentage expressed by mass relative to the dry cement mass.

[0033] In order to reduce and control the amount of entrained air in the mortar, a defoaming agent may be added. Uncontrolled higher levels of air in the mortar or concrete would reduce the mechanical strength at all ages, and increase in an uncontrolled manner the rheology of the fresh construction material.

[0034] A defoamer may for example be selected from the group consisting of mineral oils, organic polymers, surfactants and mineral mixtures, polyether siloxane and fume silica mixtures, polydimethylsiloxane and their mixtures.

[0035] Good results have been achieved with Dehydran 1922. This defoaming agent produced by BASF is a mixture of surfactants and minerals. Preferably, the construction material comprises 0.1-0.3 wt% of this additive.

[0036] The construction material used in the inventive method is a material based on a hydraulic binder, i.e. any material which produces strength-forming phases by solidifying and curing in contact with water, such as mortar or concrete. The hydraulic binder preferably comprises or is comprised of ordinary or white Portland cement. Portland cement as used in the invention may be any type of Portland cement. Suitable cements are the cements described in the European NF EN 197-1 Standard of April 2012 or mixtures thereof, preferably cement of the types CEM I, CEM II, CEM III, CEM IV or CEM V.

[0037] Good results have been achieved when using the white cement CEM I 52.5N produced at the cement plant of Le Teil, or the HTS cement produced at the cement plant of Le Teil.

[0038] Various mineral additions, such as, e.g., granulated blast-furnace slag (gbfs), fly ash, natural pozzolans, calcined clays or ground limestone, may be added to Portland cement, in order to obtain Portland composite cements. The mineral additions, typically between 10 and 50 wt.-% of the total binder weight, are in most applications ground granulated blast furnace slag, fly ash, pozzolans, ground limestone or mixtures thereof.

[0039] The water/binder ratio (wt/wt ratio) of the construction material used in the invention is preferably from 0.25 to 0.5, more preferably from 0.3 to 0.4. The water/binder ratio may vary, for example due to the water demand of the mineral additions when these are used. The water/binder ratio is defined as being the ratio by mass of the quantity of water to the dry mass of the hydraulic binder (Portland cement and mineral additions).

[0040] In a preferred embodiment the construction material is a self-levelling mortar made from sand, Portland cement, limestone filler and super-plasticizer.

[0041] The invention will now be described in more detail by reference to the following example and to an exemplary embodiment of an equipment shown in Fig. 1, which is suitable for carrying out the method of the invention.

Example 1

[0042] A mortar was prepared having the following composition:

- 2058.6 g of NAG3 Ductal premix
- 11.33 g of CHRYSO®Optima 100
- 201.7 g of water

[0043] This mortar has a slump flow of 140 mm measured according to the flow table method (ASTM C230). As the fresh mortar is self compacting, its yield stress is low and below 400 Pa.

[0044] The material was pumped at a flow rate of between 0.7 and 1.3 L/min. In the deposition head of a robot, an amount of Sika 40 AF was mixed with the mortar at a dosage of between 21 and 36 g/L of mortar.

[0045] The yield stress measured with a scissometer of the placed material was estimated between 800 and 1200 Pa.

[0046] Successive layers of the material were placed on top of each other, for a total height of approximately 1 meter, on a duration of 2 hours.

[0047] It was observed that the layers did not collapse, and the intended shape of the printed object was fully respected.

[0048] The layers were allowed to set and harden for 24 hours before the printed element could be manipulated.

Example 2

[0049] A mortar was prepared having the following composition:

- 569.3 g of white cement CEM I 52.5N Le Teil
- 350.1 g of limestone filler BL 200 from Omya
- 1004.8 g of sand Sablon 0/0.315 from Sibelco
- 11.16 g of Glenium 27 from BASF
- 270.0 g of water

[0050] This mortar has a slump flow of 210 mm measured according to the flow table Marsh Cone method (ASTM C230). As the fresh mortar is self compacting, its yield stress is low and below 400 Pa.

[0051] This formulation was tested on pumping system, without any robotic deposition device.

[0052] The material was pumped at a flow rate of 1.9L/min. In the extrusion head, Foxcrete S200 was added at a dosage of 0.4 g/L of mortar.

[0053] The yield stress of the placed material was measured at 2500 Pa.

[0054] The material was self-sustaining after the extrusion step. Up to 4 layers were put one

atop another manually after 20 min, and the layers did not collapse.

[0055] Fig. 1 shows an equipment that is suitable for carrying out the method of the invention. In Fig. 1 self-leveling mortar 1 is supplied from a storage facility or from an on-site batching plant. The mortar is conveyed to a mortar pump 2, which conveys the mortar through a pipe 3. The pipe 3 leads through a security zone 4, which comprises various connections to the pipe 3. A first connection serves to connect a rinsing water source 5 to the pipe 3 in order to clean the piping of the conveying system from time to time. Further, an emergency outlet 6 is connected to the pipe 3 for removing mortar in case of occurrence of overpressure in the pipe 3. The pressure in pipe 3 is measured by means of a pressure gauge 7. Further, a rupture disc 8 is provided, which may be designed as a non-reclosing pressure relief device that protects the pipe 3 from overpressurization.

[0056] After leaving the security zone 4 the pipe 3 leads to a robot 9, which comprises a deposition head 10. The robot 9 comprises a drive unit (not shown) that moves the deposition head 10 along a path that is determined by an electronic control module based on 3D model data for the object to be constructed. The robot 9 comprises a static mixer 11 to which the mortar is conveyed through the pipe 3. The mixer 11 serves to mix the mortar with a rheology-modifying agent that is fed to the robot 9 from a storage tank 12. The rheology-modifying agent is supplied to a pump 13, which conveys the agent through a pipe 14 to the robot 9. The pipe 14 comprises several connections that are arranged downstream of the pump 13, namely one connection for an emergency outlet 15, one connection for a rupture disc 16 and one connection for a pressure gauge 17.

[0057] The pipe 14 leads into the pipe 3 with an check valve 18 being interposed. The pressure after the mixer 11 is measured by means of a pressure gauge 19. The mixture exiting the mixer 11 may either be fed to a pipe 20 that serves to discharge a waste portion of the mixture or to a pipe 21 which leads to the deposition head for extruding the mixture through a nozzle.

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- [US2015072068A1](#) **[0002]**

Non-patent literature cited in the description

- **V.S. RAMACHANDRAN**Concrete Admixtures Handbook, Properties Science and TechnologyNoyes Publications19840000 [0029]

P a t e n t k r a v

1. Fremgangsmåde til anbringelse af et flydende byggemateriale omfattende et hydraulisk bindemiddel til bygning af strukturkomponenter lag for lag, såsom
5 til 3D-printning i beton, hvilken fremgangsmåde omfatter:
at fremføre det flydende byggemateriale til et afsætningshoved (10),
at anbringe byggematerialet gennem en udgang af afsætningshovedet (10) til
dannelse af et lag af byggemateriale,
før anbringelse af byggematerialet at tilsætte et reologi-modificerende middel
10 til byggematerialet, således at det anbragte materiale har en forhøjet flyde-
spænding, før hærdning finder sted, sammenlignet med materialet under frem-
føringstrinnet, hvor trinnet at anbringe byggematerialet omfatter at ekstrudere
byggematerialet i en pastaagtig form gennem en dyse af afsætningshovedet
(10), og hvor, efter anbringelsen af et første lag af byggematerialet, mindst et
15 efterfølgende lag af byggemateriale anbringes oven på det første lag, hvor
mængden af reologi-modificerende middel, der tilsættes til byggematerialet,
vælges således, at det øger flydespændingen, således at det første lag ikke
bryder sammen under belastningen af det mindst ene efterfølgende lag.
- 20 2. Fremgangsmåde ifølge krav 1, **kendetegnet ved at** flydespændingen af det
nyligt anbragte byggemateriale er 600 - 4.000 Pa.
3. Fremgangsmåde ifølge krav 1 eller 2, **kendetegnet ved at** byggematerialet
af det første lag får lov at hvile i et tidsrum på ikke mere end 2 minutter, for-
25 trinsvis i et tidsrum på 30-60 sek., før byggemateriale af et efterfølgende lag
anbringes oven på byggematerialet af det første lag.
4. Fremgangsmåde ifølge krav 1, 2 eller 3, **kendetegnet ved at** det reologi-
modificerende middel kontinuert tilsættes til strømmen af fremført byggema-
30 teriale.
5. Fremgangsmåde ifølge et hvilket som helst af kravene 1 til 4, **kendetegnet
ved at** det reologi-modificerende middel og byggematerialet blandes med hin-
anden før anbringelse af byggematerialet, hvor der fortrinsvis anvendes en
35 statisk blander (11) til blanding.

- 5 **6.** Fremgangsmåde ifølge et hvilket som helst af kravene 1 til 5, **kendetegnet ved at** der tilsættes et vandreduktionsmiddel, især en blødgører eller en superblødgører, fortrinsvis en blødgører baseret på polyoxypolycarboxylat eller fosphonater, til det hydrauliske bindemiddel før fremføringstrinnet, hvor fremføring af byggematerialet udføres ved pumpning.
- 10 **7.** Fremgangsmåde ifølge et hvilket som helst af kravene 1 til 6, **kendetegnet ved at** der fortrinsvis tilsættes en hærdningsaccelerator, såsom f.eks. natriumchlorid, calciumchlorid, aluminiumhydroxid, aluminiumkaliumsulfat, natriumsilicat, calciumnitrat og/eller calciumnitrit, natrium- og/eller calciumthiocyanat, til det hydrauliske bindemiddel før fremføringstrinnet.
- 15 **8.** Fremgangsmåde ifølge et hvilket som helst af kravene 1 til 7, **kendetegnet ved at** der anvendes et fortykningsmiddel eller en viskositetsforstærker som det reologi-modificerende middel.
- 20 **9.** Fremgangsmåde ifølge et hvilket som helst af kravene 1 til 8, **kendetegnet ved at** stivelsesether, celluloseether, vandopløselig polyacrylamid, kasein og/eller welangummi anvendes som eller i det reologi-modificerende middel.
- 25 **10.** Fremgangsmåde ifølge et hvilket som helst af kravene 1 til 9, **kendetegnet ved at** byggematerialet er beton eller en cementmørtel (1).
- 25 **11.** Fremgangsmåde ifølge et hvilket som helst af kravene 1 til 9, **kendetegnet ved at** byggematerialet er en beton med ultrahøj ydeevne.

DRAWINGS

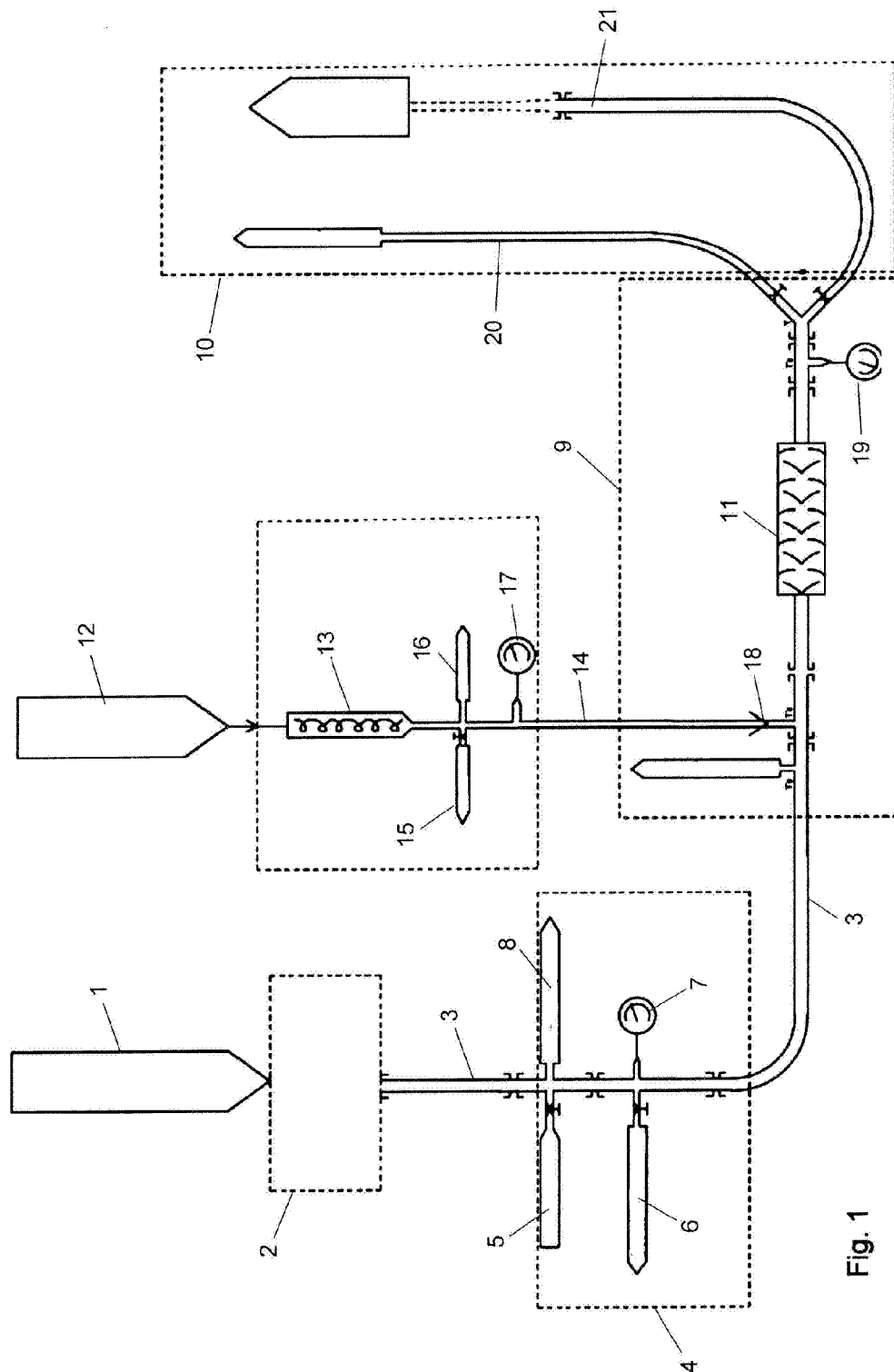


Fig. 1