(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
19 October 2017 (19.10.2017)

WIPO | PCT

(10) International Publication Number
WO 2017/177268 A1

(51) International Patent Classification:
G01N 15/08 (2006.01) *B04B 5/00* (2006.01)

(21) International Application Number:
PCT/AU2017/050321

(22) International Filing Date:
12 April 2017 (12.04.2017)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
2016901362 12 April 2016 (12.04.2016) AU

(71) Applicant: **MONASH UNIVERSITY** [AU/AU]; Wellington Road, Clayton, Victoria 3800 (AU).

(72) Inventors: **DUAN, Wen Hui**; c/- Wellington Road, Clayton, Victoria 3800 (AU). **CHEN, Shu Jian**; c/- Wellington Road, Clayton, Victoria 3800 (AU).

(74) Agent: **FPA PATENT ATTORNEYS PTY LTD**; Level 43, 101 Collins Street, Melbourne, Victoria 3000 (AU).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

— *of inventorship (Rule 4.17(iv))*

Published:

— *with international search report (Art. 21(3))*

(54) Title: CENTRIFUGE-DRIVEN INTRUSION

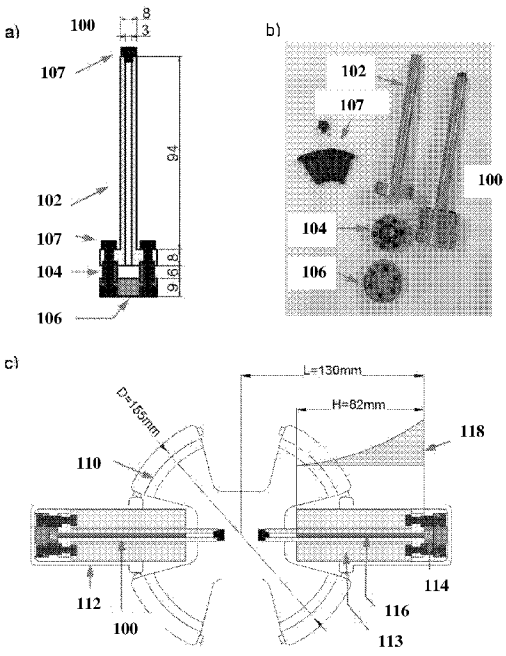


Figure 1

(57) Abstract: The invention relates to a method and substrate intrusion holder, for driving an intruding agent into pores of a porous substrate. The method includes: contacting the porous substrate with the intruding agent; and applying an intrusion pressure to the intruding agent, via centrifugation, sufficient to drive the intruding agent into pores of the porous substance. The substrate intrusion holder is adapted to be engaged with a centrifuge for driving an intruding agent into pores of a porous substrate. The substrate intrusion holder includes: a substrate holding portion defining a chamber for retaining the porous substrate in a fixed position within a substrate holding portion; a reservoir portion for storing the intruding agent, the reservoir portion having an inlet for receiving the intruding agent, and an outlet to feed the intruding agent into the substrate holding portion; and engagement means to engage the substrate intrusion holder with the centrifuge so that during centrifugation, the reservoir portion is radially closer to an axis of rotation than the substrate holding portion. There is also provided a system including, a centrifuge and the substrate intrusion holder.

WO 2017/177268 A1

Centrifuge-driven intrusion

Field of the invention

Method and apparatus for driving an intruding agent into pores of a porous substrate, such as for pore characterisation of porous materials.

Background of the invention

Pore characteristics determine many properties of porous substrates, such as mechanical properties, transport properties, creep, and shrinkage. However, the proper method for characterization of pores is still debated. The main discrepancy lies in the characterization of capillary pores, where the traditional and most frequently adopted technique is a porosimetry method such as mercury intrusion porosimetry (MIP). The porosimetry method has limitations, such as its inaccurate interpretation of pore size due to irregular and ink-bottle-like pores in cementitious materials.

Image-based characterization is often suggested for realistic observation of pores. For image analysis, the pores needs to be filled with a support material such as epoxy resin and then ground and polished to expose a flat cross-section of the material to allow imaging of the pores. The main limitation of that method is that epoxy resins have low contrast with the cementitious matrix, making it difficult to obtain clear pore images.

In the literature, the best solution for characterizing capillary pores is backscattered electro-microscope (BSE) imaging using Wood's metal as the intrusion material to fill the pores. Wood's metal has been melted at temperatures above 71 °C, driven into the pores with pressure, and cooled to harden in the pores. The use of Wood's metal to replace epoxy can significantly improve the contrast and resolution of pores under BSE imaging because of the large difference between the atomic number of the metal and that of cement.

Although the superiority of the Wood's metal intrusion has been known for decades, its application is very limited. There are extensive publications reporting the use of MIP and epoxy impregnation techniques, but only a handful of studies that have used the metal intrusion/impregnation technique. The major limitations of the Wood's

metal intrusion technique include: (1) the requirement for expensive customized high-pressure chambers and sample holder to sustain pressure; (2) the difficulty of controlling the pressure, such that customized control units are needed; and (3) the high toxicity of Wood's metal due to its Pb and Cd content creating high risk for those involved in the regular handling (grinding and polishing) of samples.

It is an object of the invention to provide a method and/or apparatus to address at least one of the problems of prior art systems.

Reference to any prior art in the specification is not an acknowledgment or suggestion that this prior art forms part of the common general knowledge in any jurisdiction or that this prior art could reasonably be expected to be understood, regarded as relevant, and/or combined with other pieces of prior art by a skilled person in the art.

Summary of the invention

In one aspect of the invention, there is provided a method for driving a liquid intruding agent into pores of a porous substrate, the method including: contacting the porous substrate with the liquid intruding agent; and applying an intrusion pressure to the liquid intruding agent, via centrifugation, sufficient to drive the liquid intruding agent into pores of the porous substance. Advantageously, the method may be used to prepare the porous substance as a sample for further characterization testing, such as SEM, other BSE analysis techniques, Micro-CT, or NMR. In such instances, the method further includes post-treatment of the sample to render it suitable for further analysis. Post-treatment may include mounting the sample, such as in epoxy resin, and/or grinding and polishing the surface and/or chemical treatment.

In an embodiment, the intruding agent is a metal or metal alloy. In this embodiment, the liquid intruding agent is a molten intruding agent, such as a molten metal or molten metal alloy. Thus, it is preferred that the intrusion process is conducted at a temperature that is greater than the melting point of the metal or metal alloy.

In one or more embodiments, the intrusion process is conducted at a temperature above the melting point of the intruding agent. In such cases where the intruding agent is a metal or a metal alloy, it is preferred that the metal or metal alloy is

a low melting point metal or a low melting point metal alloy, such as a fusible metal alloy. Where the intrusion agent is a low melting point metal or metal alloy, the inventors generally refer to this new method as centrifugation-driven low-melting-point metal intrusion (CLMI). This advantageously allows the method to be conducted at relatively low temperatures, such as at a temperature of less than about 105°C. For certain porous substrates, such as cementitious materials, damage of the pore structure can occur at temperatures of 105°C and above, for example due to dehydration of the cementitious material. Given this, it is preferred that the metal or metal alloy has a melting point that is less than about 105°C.

In embodiments where the intruding agent is a metal or metal alloy, it is further preferred that the metal or metal alloy is solid at room temperature. This is important for a number of applications, such as for characterisation of pore morphology in the porous substrate, where it is desired that the metal or metal alloy solidify in situ within the pores of the porous substrate. As such, in preferred embodiments, the method further includes solidifying the intruding agent in pores of the porous substrate, such as by lowering the temperature of the metal or metal alloy to below the melting point of the metal or metal alloy. Given this, it is preferred that the metal or metal alloy has a melting point that is greater than about 25°C so that it is able to solidify at about room temperature. Where the intruding agent is initially provided as a solid, then prior to the step of applying the intrusion pressure to the intruding agent, the method further includes heating the intruding agent to melt the intruding agent and provide the molten intruding agent.

It will be appreciated that a range of different metals or metal alloys meet these desired criteria. A range of different metal alloys can be used, suitable alloys are fusible metal alloys such as Wood's metal. However, many fusible metal alloys include toxic constituents, for example Wood's metal contains Pb and Cd which are toxic. Preferred metal alloys are those that are considered non-toxic, such as those formed from Bi, In, and Sn. Most preferably, the metal alloy is Field's metal. The use of Field's metal is particularly advantageous where the porous substrate is one which has pores that are at least about 3 nm in diameter. Generally Field's metal can be used with pores up to about 10 μm in diameter. This is because Field's metal has properties which enable it to intrude into these pores without pre-vacuuming treatment of the porous substrate, particularly when that porous substrate is a cementitious material. However, Field's

metal may still be used with pores greater than 10 microns in diameter, preferably with a pre-vacuuming step. Notwithstanding the above, prior to the contacting step, it may be advantageous to subject the porous substrate to a vacuum to remove or reduce an amount of gas within pores of the porous substrate. The removal or reduction of gases from within pores aids the intrusion process and can assist in reducing subsequent extrusion of the intruding agent from pores. This is particularly useful where pores having a diameter of greater than about 10 μm are expected.

As discussed in the background section, traditional metal intrusion processes using Wood's metal have been known for decades, but have limited application and as such have not been studied extensively due to the prevalence of MIP and epoxy impregnation techniques. Notwithstanding this, the selection of Wood's metal for those intrusion processes is due to the hardness and strength of Wood's metal. That is, Wood's metal is of sufficient strength to intrude and fill pores and then support the porous structure. Field's metal is softer than Wood's metal, and given the limited research in this space, has been avoided as a candidate for traditional metal intrusion processes in favour of Wood's metal. However, the inventors have found that Field's metal is sufficiently strong to support pore structures, particularly of cementitious materials.

In one or more embodiments, the intrusion pressure is from about 10 MPa to about 20 MPa. This intrusion pressure has been shown to provide effective intrusion of molten metal alloys, such as Wood's metal and Field's metal into pores of a porous substrate such as a cementitious material.

The desired intrusion pressure can be controlled through operation of a centrifuge, such as via setting a rotational speed of the centrifuge, as well as through the design of a substrate intrusion holder which contains both the porous substrate and the intrusion agent.

Accordingly, in another aspect of the invention, there is provided a substrate intrusion holder adapted to be engaged with a centrifuge for driving an intruding agent into pores of a porous substrate, the substrate intrusion holder including: a substrate holding portion defining a chamber for retaining the porous substrate in a fixed position within the holding portion; a reservoir portion for storing the intruding agent, the

reservoir portion having an inlet for receiving the intruding agent, and an outlet to feed the intruding agent into the substrate holding portion; and engagement means to engage the substrate intrusion holder with the centrifuge so that during centrifugation, the reservoir portion is radially closer to an axis of rotation than the substrate holding portion.

Advantageously, this substrate intrusion holder can be fitted to pre-existing standard laboratory centrifuges, allowing these to be used to control and conduct the method described above without expensive apparatus or custom-built control units. This is particularly useful for laboratory scale testing and characterisation of porous substrates, such as cementitious substrates.

In an embodiment, the substrate holding portion and the reservoir portion are separable from each other.

In an embodiment, the reservoir portion is an elongate cylindrical tube for storing the intruding agent along a length adjacent the outlet. It is preferred that the substrate holding portion is cylindrical and is arranged along a common axis with the reservoir portion. It is also preferred that the chamber has a diameter that is greater than the internal diameter of the reservoir portion. It is also preferred that the elongate tube has a length of from about 8 mm to about 12 mm. This allows the elongate tube to contain a sufficient head of liquid or molten intrusion agent such that during centrifugation, the distance between the surface of the liquid and the centre of rotation as well as the height (or head) of the intrusion agent above a surface of the substrate is such that the desired intrusion pressure is attained.

In an embodiment, the substrate holder is configured such that during centrifugation, an intrusion pressure is applied to the intruding agent sufficient to drive the intruding agent radially outward through the outlet and into pores of the porous substrate.

In an embodiment, the substrate holding portion includes a base portion, and an enclosed wall portion defining the chamber, the enclosed wall portion extending orthogonally from the base portion; wherein the base portion is separable from the enclosed wall portion to provide external access to the chamber. This arrangement is

useful so that the base can be separated from the wall portion to allow the porous substrate to be inserted into the chamber. The base portion is then reaffixed to seal the porous substrate in the chamber.

In an embodiment, the engagement means is an engagement portion having external dimensions to retain the substrate intrusion holder in the bucket of a centrifuge.

In a further aspect of the invention there is provided a system for driving an intruding agent into pores of a porous substrate, the system including: a centrifuge; and a substrate intrusion holder adapted to be engaged with a centrifuge for driving an intruding agent into pores of a porous substrate, the substrate intrusion holder including: a substrate holding portion defining a chamber for retaining the porous substrate in a fixed position within the holding portion, a reservoir portion for storing the intruding agent, the reservoir portion having an inlet for receiving the intruding agent, and an outlet to feed the intruding agent into the substrate holding portion, and engagement means to engage the substrate intrusion holder with the centrifuge so that during centrifugation, the reservoir portion is radially closer to an axis of rotation than the substrate holding portion.

In an embodiment, the centrifuge is a heated centrifuge that is configured to heat and/or maintain a temperature of the intruding agent above a melting point of the intruding agent.

In another aspect of the invention, there is provided a substrate intrusion holder adapted to be engaged with a centrifuge for driving an intruding agent into pores of a porous substrate, the substrate intrusion holder including: an elongate portion having a long axis with an inlet at one end thereof, the elongate portion having an internal tubular chamber for retaining the porous substrate in a fixed position therein and for retaining the intruding agent in contact with the porous substrate; an engagement portion for engaging the substrate intrusion holder with the centrifuge, the engagement portion being adapted to support the elongate portion and withstand pressures generated during centrifugation, such that during centrifugation, the long axis of the elongate portion is substantially aligned in the radial direction of an axis of rotation; and a sealing portion to at least seal the inlet.

The substrate intrusion holder can be formed from any material that is strong enough to resist the pressures experienced during centrifugation. Preferred materials are metals.

The elongate portion is described as having an internal tubular chamber. This chamber may be of any cross-sectional shape. However, in preferred embodiments, the chamber has a polygonal cross-section, and more preferably a square or rectangular cross-section. This is useful as it aids in retaining the porous substrate in position once loaded into the internal chamber.

In an embodiment, the elongate portion, the engagement portion, and the cap are three separable components that are assembled together to form the substrate intrusion holder. In such embodiments, the engagement portion has an internal cavity that is sized to receive the elongate portion entirely within. The internal cavity of the engagement portion is adapted to receive the elongate portion so that external walls of the elongate portion are in contact with internal walls of the internal cavity of the engagement portion. In this embodiment, the cap portion additionally holds the elongate portion within the engagement portion.

In an embodiment, the engagement portion has external dimensions to retain the substrate intrusion holder in the bucket of a centrifuge.

In still a further aspect of the invention, there is provided a system for driving an intruding agent into pores of a porous substrate, the system including: a centrifuge; and a substrate intrusion holder adapted to be engaged with a centrifuge for driving an intruding agent into pores of a porous substrate, the substrate intrusion holder including: an elongate portion having a long axis with an inlet at one end thereof, the elongate portion having an internal tubular chamber for retaining the porous substrate in a fixed position therein and for retaining the intruding agent in contact with the porous substrate; an engagement portion for engaging the substrate intrusion holder with the centrifuge, the engagement portion being adapted to support the elongate portion and withstand pressures generated during centrifugation, and such that during centrifugation, the long axis of the elongate portion is substantially aligned in the radial direction of an axis of rotation; and a sealing portion to at least seal the inlet.

Further aspects of the present invention and further embodiments of the aspects described in the preceding paragraphs will become apparent from the following description, given by way of example and with reference to the accompanying drawings.

Brief description of the drawings

Figure 1: a) Overview of container design (assembly of 3 parts), b) the container parts before assembly, and c) schematic diagram of intrusion pressure

Figure 2: Typical BSE images of Wood's metal intruded samples: a) sample W1; a-insert, magnified BSE image of pores near an unhydrated cement grain; c) sample W2; c-insert, magnified BSE image of large metal-filled pores. Typical binary images of pores (black) in (b) sample W1 and (d) sample W2. The inserts in b) and d) show the greyness spectra and the threshold value of the greyness (0-255) above which are the pores (percentage indicates the fraction of pixels above the threshold).

Figure 3 a) BSE images of Field's metal intruded samples, b) magnified view of extrusion from large pores, c) BSE image with the extrusion areas excluded, and d) binary image of pores excluding the extruded area.

Figure 4: Data comparison between Wood's metal and Field's metal intrusion: a) 28-day samples with w/c=0.4, b) 7-day samples with w/c=0.8.

Figure 5: BSE images of pre-vacuumed mortar samples prepared by CMLI method.

Figure 6: Schematic of extrusion process of intruded metal in large pores: a) metal in pore before extrusion, b) metal extruded by shear failure of metal, and c) metal extruded by bonding failure with cement.

Figure 7: Photograph showing an embodiment of a sample holder.

Figure 8: Schematic illustrating radial intrusion pressure gradient on an elongated sample.

Figure 9: Radiographic results of a sample as a function of the intrusion pressure gradient.

Detailed description of the embodiments

The invention relates to methods and apparatus' for driving an intrusion agent into pores of a porous substance. It will be appreciated that the invention may be used with a range of different intrusion agents and porous substances. However, the preferred form of the invention relates to a molten metal intrusion agent and a porous cementitious material, particularly for the purpose of characterising the pore morphology of that cementitious material.

More particularly, the invention is described in relation to the intrusion behaviour of a non-toxic low-melting-point metal using centrifugation to develop a better pore characterization technique for cementitious materials such as ordinary Portland cement. Centrifugation is a safe and effective method for driving melted low-melting-point alloys into cementitious material at pressure between 10 to 20 MPa, and more particularly 12 to 15 MPa. While toxic metals and metal alloys may be used, the preferred intrusion agent is the non-toxic Field's metal alloy. For pores between 100 nm to 10 μm, Field's metal can be used without vacuuming the sample before intrusion. For pores greater than 10 μm, pre-vacuuming of the sample is suggested to prevent the extrusion of hardened Field's metal from large pores. Different failure modes for the extrusion phenomenon were analyzed and, without wishing to be bound by theory, the inventors are of the view that weak bonding between the Field's metal and the cement matrix is the main cause for this extrusion.

Materials and instrumentation

Type GP ordinary Portland cement conforming to the requirements of Australian Standard AS 3972 was used. Wood's metal and Field's metal were purchased from Rotometals, Inc. The relevant chemical composition and physical properties are listed in Table 1. Field's metal is proposed as an alternative low-melting-point metal for intrusion, as it is non-toxic, containing neither lead nor cadmium.

Table 1 Properties of Wood's metal and Field's metal.

	Composition by weight	Melting point	Contact angle	Yield strength	Density

Wood's metal	50%cBi, 26.7% Pb, 13.3% Sn, 10% Cd	70 °C	130°*	~60 MPa	9.38g/cm^3
Field's metal	32.5% Bi, 51% In, 16.5% Sn	62 °C	130°*	<33.4 MPa	8 g/cm^3

* due to limited information on contact angle for low melting point metals, they are assume to have similar contact angle as mercury.

An Eppendorf Centrifuge 5702 with the swing bucket rotor A-4-38 was used. A Nova 450 SEM was used to perform BSE imaging of the sample. Two containers were designed to hold the sample and high-pressure molten metal in place. Assembly of the container 100 is shown in **Figure 1a** and **Figure 1b**. The container was composed of three parts. Part 1 102 includes a tube to raise the pressure head of the molten metal at the top seal of the sample chamber. Part 2 104 is the chamber in which the cement sample is seated. Part 3 106 is the bottom seal of the sample chamber. These three parts were made of high strength 2024 aluminum alloy and assembled using 6 M4 screws 107 made of high tensile steel. The top of the tube was threaded and sealed using a short M4 screw 107 to prevent spillage. The container 100 can be cleaned in a hot water bath and reused.

Sample preparation and centrifuge intrusion process

Two mixes of ordinary Portland cement (OPC) paste and one mix of OPC mortar were cast into 20 mm cubes with the water to cement (w/c) ratios of 0.4 and 0.8. No additive was used in the three mixes. Specimens were demoulded after 16 hours. Then the w/c=0.4 samples and the w/c=0.8 samples were cured in saturated calcium hydroxide solution for 28 days and 7 days, respectively. The cured samples were then placed in ethanol to stop hydration. The cement pastes were sectioned and trimmed into the approximate size of 5mm by 5mm by 5mm with ethanol as the coolant and lubricant. The cement samples were reserved in vacuum for one week to remove liquid from the pores.

The centrifuge was used to provide the high pressure for the liquid metal to intrude into the pores of the cement samples. A schematic diagram of the system is illustrated in **Figure 1c**. **Figure 1c** illustrates a centrifuge 110, with a container 100 held within a centrifuge bucket 112 with plastic foam 113. An OPC sample 114 is provided at

the end of the container that is farthest from the centre of rotation of the centrifuge 110 during operation. A melted metal intruding agent is provided 116. The pressure gradient of melted metal 118 is illustrated along a length of the container 100. The intrusion pressure P acting on the sample 114, measured in MPa, was calculated as:

$$P = \frac{1}{2}\rho\omega^2\left(2L_1H + H^2\right)/10^9 \qquad 1$$

where ρ is the density of liquid metal, with the value of 9.8g/cm^3 for Wood's metal and 8g/cm^3 for Field's metal, ω is the centrifuge speed measured in rad/s. L_1 = 48mm, is the distance from the center of the centrifuge to the surface of the liquid metal in the tube, H =82 ± 2mm, is the depth of liquid metal in relation to the surface of the cement sample.

The CLMI consisted of the following steps:

(1) Cement samples were seated in the chamber of the tube and the three parts of the tube were assembled with M4 screws, leaving the top open.

(2) The tubes were then preheated to above 90°C in a water bath. The liquid metal gradually filled into the tube from the top as the metal particles melted. The bath was sealed to prevent water entering the container.

(3) When the depth of the metal reached 82±2 mm, the tube was sealed. The tubes were wrapped in foam plastic and seated into the centrifuge buckets.

(4) The sets were heated in the water bath to maintain the temperature above 90°C for 5 min and then centrifuged. The centrifuge time was set at 10 minutes to allow complete solidification of the liquid metal during the centrifugation process.

(5) The top screws of the sets were reopened and the vacant depth of the metal was refilled to the level of 82±2 mm (as in step 3) to compensate for the volume intruded into the sample.

(6) Step 4 was repeated. For pre-vacuumed samples, step (2) was performed in a vacuum oven with the container filled with metal particles and then melted under the vacuum.

Four samples were intruded, as listed in Table 2. W1 and W2 are samples intruded with Wood's metal while F1, F2 and F3 are samples intruded with Field's metal. F3 is a mortar sample with quartz sand as the fine aggregate and the rest of the samples are paste sample with no sand. The centrifuge speed was set at 4400 RPM, which, based on Equation 1, provides an intrusion pressure of 15.2 ± 0.34 MPa and 12.4 ± 0.28 MPa for Wood's metal and Field's metal respectively. The centrifuge time was set at 10 minutes so that the liquid metal could completely harden during the centrifuge process. The intruded samples were removed from the chambers of the tubes and preserved in a vacuum oven and dried for 24 hours.

Table 2: Sample information

Sample Name	w/c	Age (Days)	sand/cement	Centrifuge Speed (RPM)	Intrusion Pressure (MPa)
W1	0.4	28	0	4400	15.2 ± 0.34
W2	0.8	7	0	4400	15.2 ± 0.34
F1	0.4	28	0	4400	12.4 ± 0.28
F2	0.8	7	0	4400	12.4 ± 0.28
F3	0.5	28	2	4400	12.4 ± 0.28

Table 3 below provides a summary showing the relationship between of intrusion pressure and rotation speed for Field's metal.

Table 3: Relationship between pressure and rotation speed

Rotation speed (RPM)	Radius of gyration (mm)	Depth of metal (mm)	Pressure (MPa)
200	130	82	0.03
1000	130	82	0.64
3000	130	82	5.76
4400	130	82	12.40
8000	130	82	40.98
10000	130	82	64.03
20000	130	82	256.10
30000	130	82	576.23

In comparison with the traditional external-pressure-driven methods, a unique advantage of using centrifugation as the driving force of the intrusion is that a gradient

pressure can be applied on the sample. This requires a specially adapted sample holder. **Figure 7** is an embodiment of a specially adapted sample holder. This sample holder comprises three primary components: (i) a holder 700 which is designed to be inserted into a bucket of a centrifuge and is sufficiently robust to accommodate the high pressures during centrifugation, (ii) a cap 702, and (ii) a long hollow insert 704 for receiving a sample of the porous substrate and the intrusion agent. In this case, each of these components is formed from plastic via a 3D printing process.

In this embodiment, the holder 700 has an external diameter of about 38mm and a length of about 120nn. The holder 700 has an internal diameter which is sized to receive the hollow insert 704. The holder 700 has a body part 708 which is configured to engage with the centrifuge. In this case, the body part 708 is sized so that it fits tightly into a centrifuge bucket. The holder 700 also includes a threaded portion 710 to which the cap 702 can be attached.

The hollow insert 704 has a square cross-sectioned inner cavity that is about 10 mm x 10 mm, and has a central axis 706 that runs along its length. In use, a porous substrate is placed within the hollow insert 704 along the axial length in such a manner that the intrusion agent can be placed within the hollow insert 704 in contact and adjacent with the porous substrate along the length of the hollow insert 704. By way of example, the hollow insert 704 may be half-filled with the porous substrate along its length direction – that is, with reference to **Figure 7** the hollow insert may be filled with the porous substrate along its length from a side wall parallel with the central axis to the central axis 704, the remaining space i.e. the half volume from the central axis 706 to the opposite parallel side wall is then filled with the intrusion agent. The hollow insert 704 (now filled with porous substrate and intrusion agent) is inserted within the holder 700 and the cap 702 is applied to seal the hollow insert 704 within the holder 700. Holder 700 is then placed within a bucket of a centrifuge.

Once centrifugation has commenced, the rotation causes the sample holder to be oriented such that the central axis 706 is substantially aligned in the radial direction. As the intrusion pressure varies with distance from the centre of rotation, the porous substrate experiences different intrusion pressures along its length, e.g. the porous sample experiences a pressure gradient. This is explained in more detail below.

When an elongated sample is immersed in melted metal and subjected to the centrifugal forces as shown in **Figure 1**, different pressure is applied simultaneously on the sample. This is further illustrated in **Figure 8. Figure 8** shows a centrifuge 800 with an elongate sample 802 held in a sample holder 804 which in turn is held within a centrifuge bucket 807 of the centrifuge 800 with plastic foam 804. As can be seen the intrusion pressure 806 of an intruding agent 808 (in this case a molten metal) increases with radial distance from the centre of rotation of the centrifuge (e.g. pressure gradient increases as a function of radial distance), and is greatest at the end of the sample farthest from the centre of rotation.

The effect of this pressure gradient on the intrusion of an intruding agent (such as a metal or metal alloy) into a sample can be observed with a range of techniques, including x-ray imaging or micro-CT scanning. In x-ray imaging, the sample surface is perpendicularly irradiated with x-rays by an emitter. X-rays penetrate through the sample and are detected by an x-ray detector. The intruding agent (in this case a metal) and the sample components have different atomic numbers which results in differential adsorption of x-rays. The metal, having a higher relative atomic number than the sample, absorbs x-rays more efficiently than the sample components, thus reducing the intensity of x-rays reaching the x-ray detector located behind the sample. In contrast, areas of the sample with less or no metal provide a lower barrier to x-ray transmission, thus allowing a comparatively higher intensity of x-rays to reach the x-ray detector. This difference in relative x-ray intensity can be used to determine the amount of intruded metal along the radial length of the sample. **Figure 9** provides a grayscale radiograph 900 showing the difference in x-ray intensity as a function of intrusion pressure gradient 902. The sample includes a first end 904 and a second end 906. The first end 904 is nearer to the centre of rotation than the second end 906, and as such experiences a lower intrusion pressure than the second end 906 (as indicated in the depiction of the pressure gradient 902). The radiograph 900 shows the first end 904 being darker than the second end 906. This indicates that a smaller amount of metal has intruded into the first end (the presence of a smaller relative amount of intruded metal having a low x-ray blocking efficiency thus resulting in the darker colouration in the radiograph) than in comparison with the second end 906 (the presence of a larger relative amount of intruded metal preventing transmission of a higher proportion of x-rays resulting in brighter colouration in the radiograph).

The volume of the intruded metal can be calculated by comparing the brightness in the radiograph 900 (see **Figure 9**). The pore size distribution of the sample can be calculated based on the pressure-pore size relationship (e.g. the Washburn's Equation used in mercury intrusion porosimetry) and the variation of intruded volume (brightness) in y direction. In addition, intruded volume (brightness) of metal can vary in x direction due to different connectivity of pores. Compared with mercury intrusion porosimetry, the gradient pressure metal intrusion is based on the same principle, but has advantages including the ability to measure pore connectivity, as well as providing a method that is time-saving, non-toxic, and of lower cost.

BSE images and image analysis

The intruded samples were mounted in epoxy resin and then lapped and ground using silicon carbide papers down to grit P1000 to expose cross-sections of the samples. The intruded samples were then subsequently polished for 30 minutes using diamond pastes in the grades of 60 μm, 25 μm, 6 μm, 1 μm, 0.25 μm, and 0.1μm. Before moving to a finer grit, each sample was immersed into ethanol and cleaned in an ultrasonic bath remove any dirt on the surface. Finally, each sample was dried in a vacuum for 24 hours. Then the samples were coated with a thin layer of carbon to prevent for charging under BSE microscopy. Samples were observed and imaged under BSE microscopy at the magnification of 1000× and at the acceleration voltage of 5KV. Five images were taken randomly at the center of each sample providing data of more than 50,000 pores on each sample.

The BSE images were further analyzed by Image-J. First, the scale was set based on the scale bar on the BSE image. The contrast of the image was enhanced, allowing 0.4% of the pixels to become saturated. Then the image data was converted into 8-bit grayscale, with the range of greyness 0-255. Binary images of the pores were obtained by thresholding using IsoData algorithm. The intruded pores, identified as black pixels in the binary image, were analyzed using the inbuilt algorithm of Image-J. A scaling factor was set for each pixel based on BSE. Solid inclusions (white pixels) within pores were considered in the calculation of pore sizes. Pores at the edges of the image were ignored as their profiles were incomplete.

CLMI using Wood's metal and the non-toxic Field's metal

Figure 2a and **Figure 2c** show typical BSE images for CLMI for samples with different pore characteristics. These images were obtained using low-energy electrons and ultra-long electron beam dwell time (45 μs) to enhance the elemental contrast and resolution of pores, facilitating easy identification of the pores via computer-aided image analysis. A clear difference can be seen between the pores in **Figure 2a** and **Figure 2c**. **Figure 2a** shows the cement paste that was hydrated for 28 days with the water to cement ratio of 0.4. It can be seen that the sample possesses mainly small pores with diameter less than a few hundred nm. More large pores are observed in the cement paste hydrated for 7 days with the water to cement ratio of 0.8 in **Figure 2c**). A zoomed-in view (**Figure 2a**) insert) of the pores surrounding an unhydrated cement grain demonstrates the distribution of fine-metal-filled pores in detail. For the large pores in the 0.8, 7-day sample, the images (**Figure 2c**) insert) clearly show the curved and complex shape of pore perimeters.

As demonstrated in **Figure 2b** and **Figure 2d**, the analysis can successfully distinguish the pores (black) from the cement (white) based on the IsoData threshold method. The threshold line is shown in the greatness spectra in **Figure 2b** and **Figure 2d**, and it indicates that the cement matrix (high peaks to the left of the threshold line) can be easily separated from the pores (to the right of the threshold line). CLMI was also applied using Field's metal rather than Wood's metal. **Figure 4a** shows the BSE of the Field's metal method. The Field's metal intruded samples show similar resolution and contrast to the Wood's metal intruded samples.

However, extrusion of the Field's metal is observed at some pores. As shown in **Figure 3a** and in the magnified view in **Figure 3b**, the extruded metal seems to have been squeezed out of the pores plastically. This extrusion phenomenon of solid metal phase is an interesting finding as discussed above. For pore analysis, these areas with extruded pores can be excluded from the analysis, as shown in **Figure 3c** and **Figure 3d**. Then the cumulative pore size distribution curves (F curve) can be obtained using the same protocol as for Wood's metal. The F curves for the Field's metal intruded samples are shown and compared with the Wood's metal intruded samples in **Figure 4a** and **Figure 4b**.

Figure 4a shows that for the 28-day w/c = 0.4 sample, the *F* curve of the Field's metal intruded sample overlaps with that of the Wood's metal intruded sample. The observable range of the pore diameter is from around 0.1 um to 10 um, about two orders of magnitude. In the 7-day sample with w/c = 0.8, the *F* curve of the Field's metal intruded sample overlaps with that of the Woods' metal intruded sample when d_p is smaller than around 9 um. When d_p is greater than 9 um, the Field's metal intruded samples display lower porosity. This is due to the exclusion of the extruded area, as the extrusion phenomenon is found to affect mainly large pores, as shown in **Figure 4a**. The higher intrusion pressure of the Wood's metal (15.2 MPa) does not result in an increase in the observable small pores. This indicates that pressure around 12 MPa is sufficient for filling pores for BSE imaging.

In general, the results show that Field's metal is a superior replacement for the toxic Wood's metal if pores with d_p less than 10 um are of interest. For observation of large pores, Field's metal can also be used with a pre-vacuum approach to eliminate the extrusion effect, as discussed below.

Effect of vacuum on the intrusion process

There are two possible causes for the extrusion observed: one is the pressure of gas trapped inside the pores; the other is the shrinkage of the matrix due to drying or relaxation of the stress generated during intrusion. To determine which of these was the dominant cause, the effect of pre-vacuuming on the extrusion phenomenon was investigated. **Figure 5a** and **Figure 5b** present typical BSE images of a pre-vacuumed mortar sample that contains a significant amount of large pores (d>10 μm) and it shows that extrusion can be mostly eliminated by the pre-vacuuming. However, the pre-vacuum technique causes some cracks, as shown in **Figure 5a**, due to the loss of water at high vacuum and temperature. Besides the cracks, the method still allows a clear view of the large pores such as in the interfacial transition zones (ITZ) shown in **Figure 5a**).

The pre-vacuumed samples indicate that that the gas trapped inside the pore is the dominant cause of the extrusion. For better understanding of the extrusion phenomenon, the mechanism is studied here. **Figure 6** illustrates the extrusion process of the metal with two possible failure modes, shear failure (see **Figure 6b**)in the metal

and bonding failure between the metal and the cement matrix (see **Figure 6c**). Here, the intrusion considered is in atmosphere and in an ideal cylindrical pore. As shown in **Figure 3a** and **Figure 3b**, no OPC particles are attached to the extruded metal indicating that there has been no failure in the cement matrix. Assuming that the gas trapped at the end of the pore in **Figure 6a** has a pressure of P_G, the extruding force acting at the bottom of the metal is:

$$N_{ex} = 0.25\pi P_G\left(d_p - 2t\right)^2 \qquad 2$$

where N_{ex} is the extruding force, t is the thickness of metal attached to the cement after extrusion. If the extrusion is due to bonding failure, then t = 0. If the extrusion is due to shear failure of the metal, t is a variable depending on the amount of N_{ex} and the shear resistance of metal S, given as:

$$S = \sigma_\gamma pL \qquad 3$$

where σ_γ is the shear strength of the metal, L is length of the pore, and p is the perimeter of the failure surface. If the extrusion is cylindrical, p equals $\pi(d_p-2t)$.

The force equilibrium during the intrusion process can be estimated based on Washburn's equation as:

$$P_L - P_G = -\frac{4\gamma\cos\theta}{d_p} \qquad 4$$

where P_A is the atmosphere pressure, V_i and V_f are the volume of the gas in the pore before and after the intrusion respectively. It is shown that for pores with d_p greater than 3 um, P_G/P_L is greater than 95% and V_f/V_i is less than 1% when P_L =12.4 MPa. For such pores, therefore, one can assume that $P_G = P_L$ =12.4 MPa and V_f is negligible. The criterion for shear failure in the metal can be found by making $N_{ex} = S$ and P_G =12.4, giving:

$$\frac{L}{d_p - 2t} < \frac{12.4\,\text{MPa}}{4\sigma_\gamma} \qquad 5$$

It can be seen from Equation 5 that wide and shallow pores can be more easily extruded. Based on Table 1, σ_γ of Wood's metal and Field's metal can be assume to be around 60 and 30 MPa respectively. This indicates that only very shallow pores with L/d_p-$2t$ < 0.1 may be subject to shear failure. Such pores may easily be removed during polishing of the sample and thus would not be visible in BSE observation. Thus, the calculations here indicate that the observed extrusion phenomenon is not due to shear failure of the metal.

Therefore, bonding failure is the preferred failure mode. The bonding resistance R is given as:

$$R = \tau p L \qquad 6$$

where τ is the interfacial shear strength between the metal and the matrix. The failure criterion is obtained by making $N_{ex} = S$ and P_G =12.4, giving:

$$\frac{L}{d_p} < \frac{12.4\,\text{Mpa}}{4\tau} \qquad 7$$

From observation of extruded metal strips, the maximum L/d_p observed is around 15, giving an estimation of τ =0.2 MPa. This indicates that Field's metal interacts very weakly with the cement matrix when hardened. In contrast, Wood's metal tends to have very strong bond resistance with the cement matrix, preventing the extrusion phenomenon. Using Equation 7, τ needs to be greater than around 3.1 MPa to resist the extrusion of pores with L/d_p >1.

Given the above, and without wishing to be bound by theory, the inventors are of the view that extrusion is not due to the lower strength of Field's metal but due to the weak bonding between Field's metal and the cement matrix. This finding indicates that intrusion and extrusion using Field's metal may induce less damage to pores due to the advance and withdrawal of metal. For that reason, Field's metal is a good candidate for studying the hysteresis of the intrusion/extrusion process.

Conclusion

The results demonstrate that centrifugation is a safe and effective method for providing and controlling pressure of melted liquid alloys for intrusion into cementitious samples. The BSE image of the processed sample demonstrates high resolution and contrast of pores, with an observation range from around 100 nm to 10 μm. The results suggest that the intrusion pressure of around 12 MPa is adequate to fill pores for BSE imaging. Almost identical cumulative pore diameter distribution curves were found for Field's metal and Wood's metal intruded samples between 100 nm and 10 μm, indicating that Field's metal can replace Wood's metal for observation of pores in this range. For pores greater than 10 μm, the phenomenon of extrusion is observed with Field's metal, but can be eliminated by pre-vacuuming the sample. Analysis of the extrusion mechanism indicates that it is attributable to the weak bonding between the Field's metal and the cement matrix.

It will be understood that the invention disclosed and defined in this specification extends to all alternative combinations of two or more of the individual features mentioned or evident from the text or drawings. All of these different combinations constitute various alternative aspects of the invention.

CLAIMS

1. A method for driving an intruding agent into pores of a porous substrate, the method including:

contacting the porous substrate with the intruding agent; and

applying an intrusion pressure to the intruding agent, via centrifugation, sufficient to drive the intruding agent into pores of the porous substance.

2. The method of claim 1, wherein the intruding agent is a metal or metal alloy.

3. The method of claim 2, wherein the metal or metal alloy is a low melting point metal or a low melting point metal alloy.

4. The method of claims 2 or 3, wherein the metal or metal alloy is solid at room temperature.

5. The method of claims 2 or 3, wherein the metal or metal alloy has a melting point that is greater than about 25°C and less than about 105°C.

6. The method of any one of the preceding claims, wherein the method further includes solidifying the intruding agent in pores of the porous substrate.

7. The method of any one of the preceding claims, wherein prior to the contacting step, the method further includes subjecting the porous substrate to a vacuum to remove or reduce an amount of gas within pores of the porous substrate.

8. The method of any one of the preceding claims, wherein the intruding agent is a solid, and prior to the step of applying the intrusion pressure to the intruding agent, the method further includes heating the intruding agent to melt the intruding agent.

9. The method of any one of claims 1 to 8, wherein contacting the porous substrate with the intruding agent prior to contacting the porous substrate with the intruding agent, the method further includes providing the intruding agent in molten form.

10. The method of any one of the preceding claims, wherein the intrusion pressure is from about 10 MPa to about 20 MPa.

11. A substrate intrusion holder adapted to be engaged with a centrifuge for driving an intruding agent into pores of a porous substrate, the substrate intrusion holder including:

a substrate holding portion defining a chamber for retaining the porous substrate in a fixed position within a substrate holding portion;

a reservoir portion for storing the intruding agent, the reservoir portion having an inlet for receiving the intruding agent, and an outlet to feed the intruding agent into the substrate holding portion; and

engagement means to engage the substrate intrusion holder with the centrifuge so that during centrifugation, the reservoir portion is radially closer to an axis of rotation than the substrate holding portion.

12. The substrate intrusion holder of claim 11, wherein the substrate holding portion and the reservoir portion are separable from each other.

13. The substrate intrusion holder of claim 11 or 12, wherein the reservoir portion is an elongate hollow cylindrical tube for storing the intruding agent along a length adjacent the outlet.

14. The substrate intrusion holder of claim 13, wherein the elongate hollow cylindrical tube has a length of from about 8 mm to about 12 mm in length.

15. The substrate intrusion holder of claim 13, wherein the substrate holding portion is cylindrical and is arranged along a common axis with the reservoir portion.

16. The substrate intrusion holder of claim 14, wherein the chamber has a diameter that is greater than the internal diameter of the reservoir portion.

17. The substrate intrusion holder of any one of claims 11 to 16, wherein the substrate holding portion includes:

a base portion, and

an enclosed wall portion defining the chamber, the enclosed wall portion extending orthogonally from the base portion;

wherein the base portion is separable from the enclosed wall portion to provide external access to the chamber.

18. A substrate intrusion holder of any one of claims 11 to 17, configured such that during centrifugation, an intrusion pressure is applied to the intruding agent sufficient to drive the intruding agent radially outward through the outlet and into pores of the porous substrate.

19. A system for driving an intruding agent into pores of a porous substrate, the system including:

a centrifuge; and

a substrate intrusion holder adapted to be engaged with a centrifuge for driving an intruding agent into pores of a porous substrate, the substrate intrusion holder including:

a substrate holding portion defining a chamber for retaining the porous substrate in a fixed position within the holding portion,

a reservoir portion for storing the intruding agent, the reservoir portion having an inlet for receiving the intruding agent, and an outlet to feed the intruding agent into the substrate holding portion, and

engagement means to engage the substrate intrusion holder with the centrifuge so that during centrifugation, the reservoir portion is radially closer to an axis of rotation than the substrate holding portion.

20. The system of claim 19, wherein the centrifuge is a heated centrifuge that is configured to heat and/or maintain a temperature of the intruding agent above a melting point of the intruding agent.

21. A substrate intrusion holder adapted to be engaged with a centrifuge for driving an intruding agent into pores of a porous substrate, the substrate intrusion holder including:

an elongate portion having a long axis with an inlet at one end thereof, the elongate portion having an internal tubular chamber for retaining the porous substrate in a fixed position therein and for retaining the intruding agent in contact with the porous substrate;

an engagement portion for engaging the substrate intrusion holder with the centrifuge, the engagement portion being adapted to support the elongate portion and withstand pressures generated during centrifugation, such that during centrifugation, the long axis of the elongate portion is substantially aligned in the radial direction of an axis of rotation; and

a sealing portion to at least seal the inlet.

22. A system for driving an intruding agent into pores of a porous substrate, the system including:

a centrifuge; and

a substrate intrusion holder adapted to be engaged with the centrifuge for driving an intruding agent into pores of a porous substrate, the substrate intrusion holder including:

an elongate portion having a long axis with an inlet at one end thereof, the elongate portion having an internal tubular chamber for retaining the porous substrate in a fixed position therein and for retaining the intruding agent in contact with the porous substrate;

an engagement portion for engaging the substrate intrusion holder with the centrifuge, the engagement portion being adapted to support the elongate portion and withstand pressures generated during centrifugation, such that during centrifugation, the long axis of the elongate portion substantially aligned in the radial direction of an axis of rotation; and

a sealing portion to at least seal the inlet.

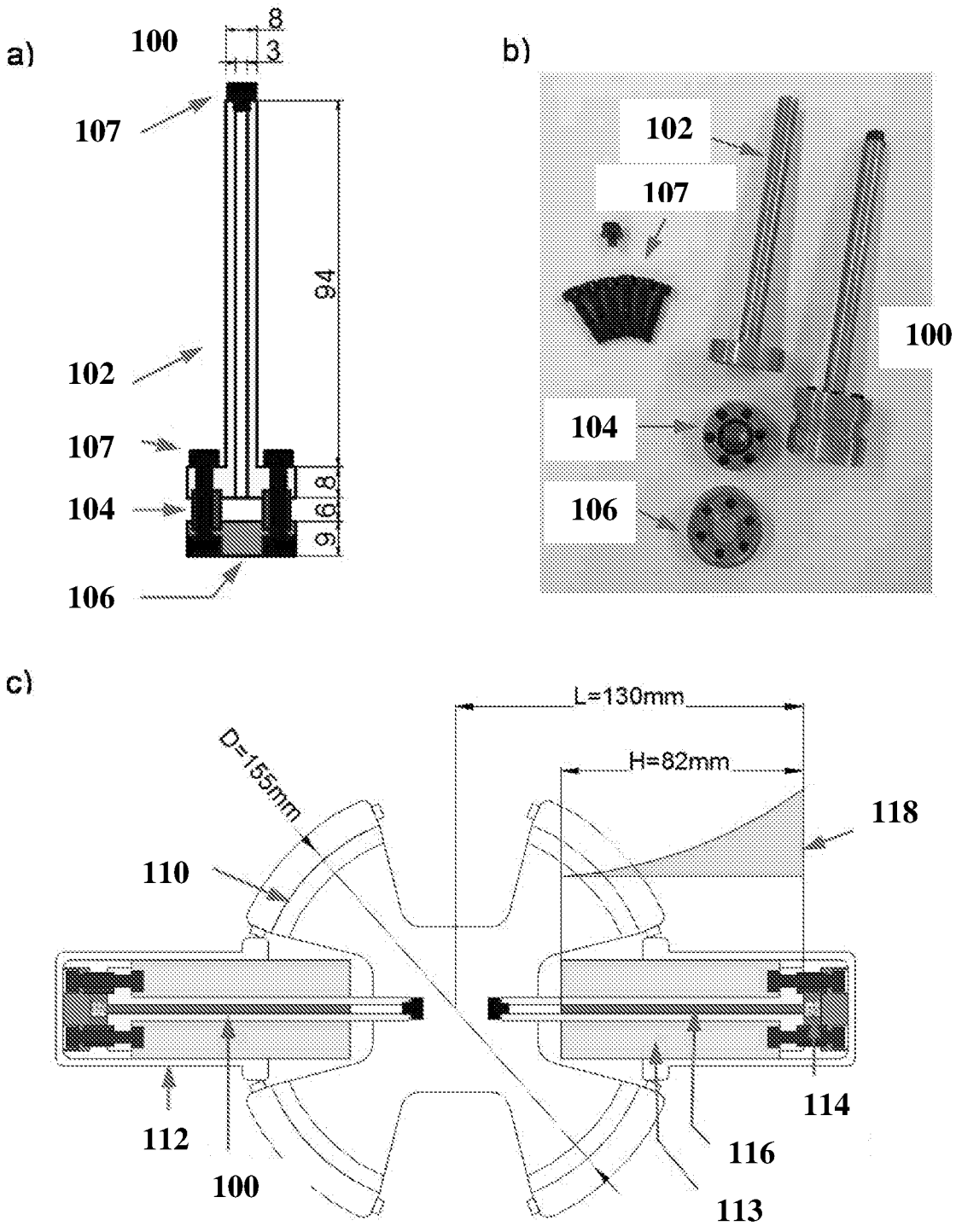

a)
100
8
3
107
94
102
107
104
8
6
9
106
b)
102
107
100
104
106
c)
L=130mm
H=82mm
D=155mm
118
110
112
100
114
116
113

Figure 1

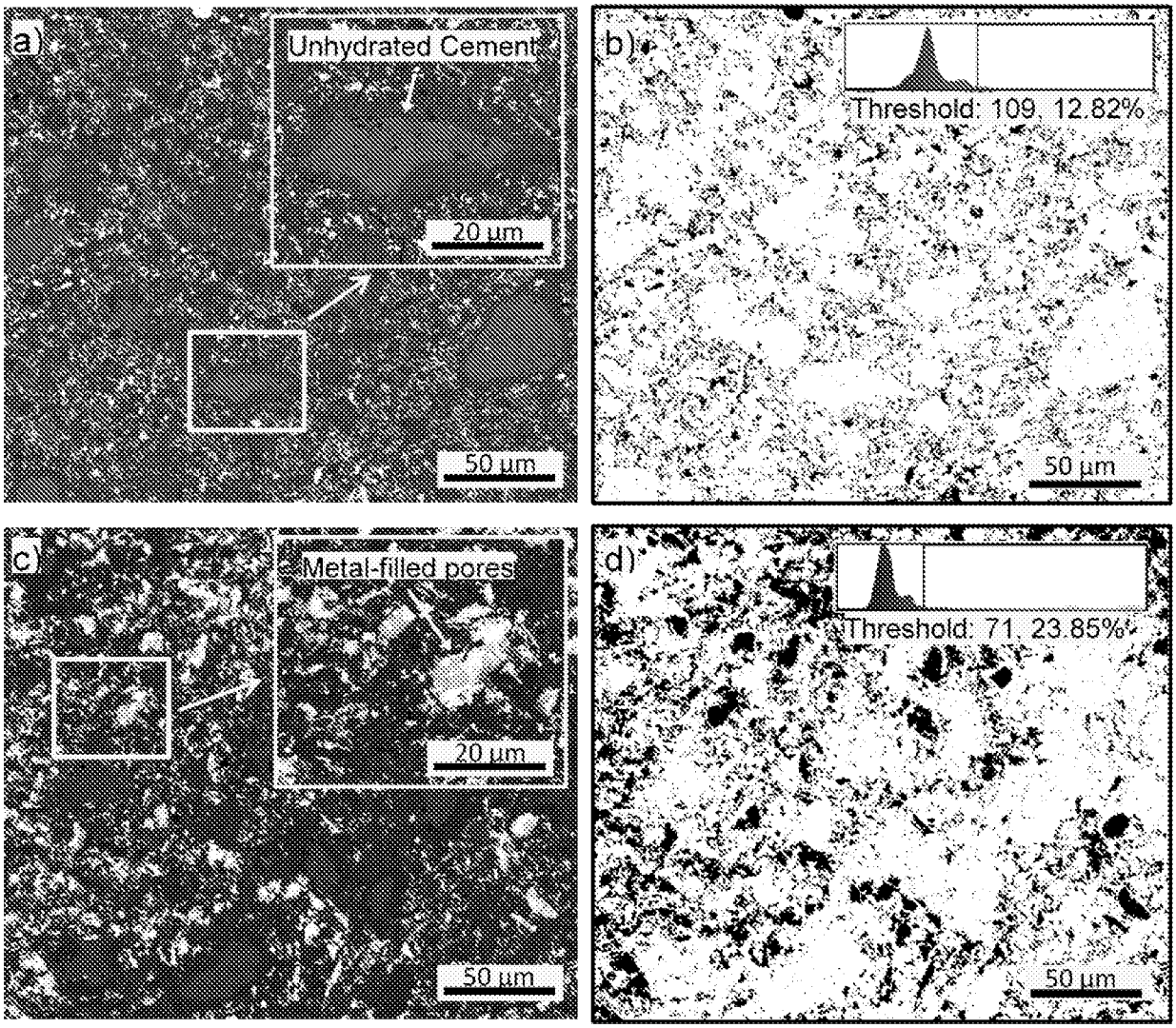

a)
Unhydrated Cement
20 µm
50 µm
b)
Threshold: 109, 12.82%
50 µm
c)
Metal-filled pores
20 µm
50 µm
d)
Threshold: 71, 23.85%
50 µm

Figure 2

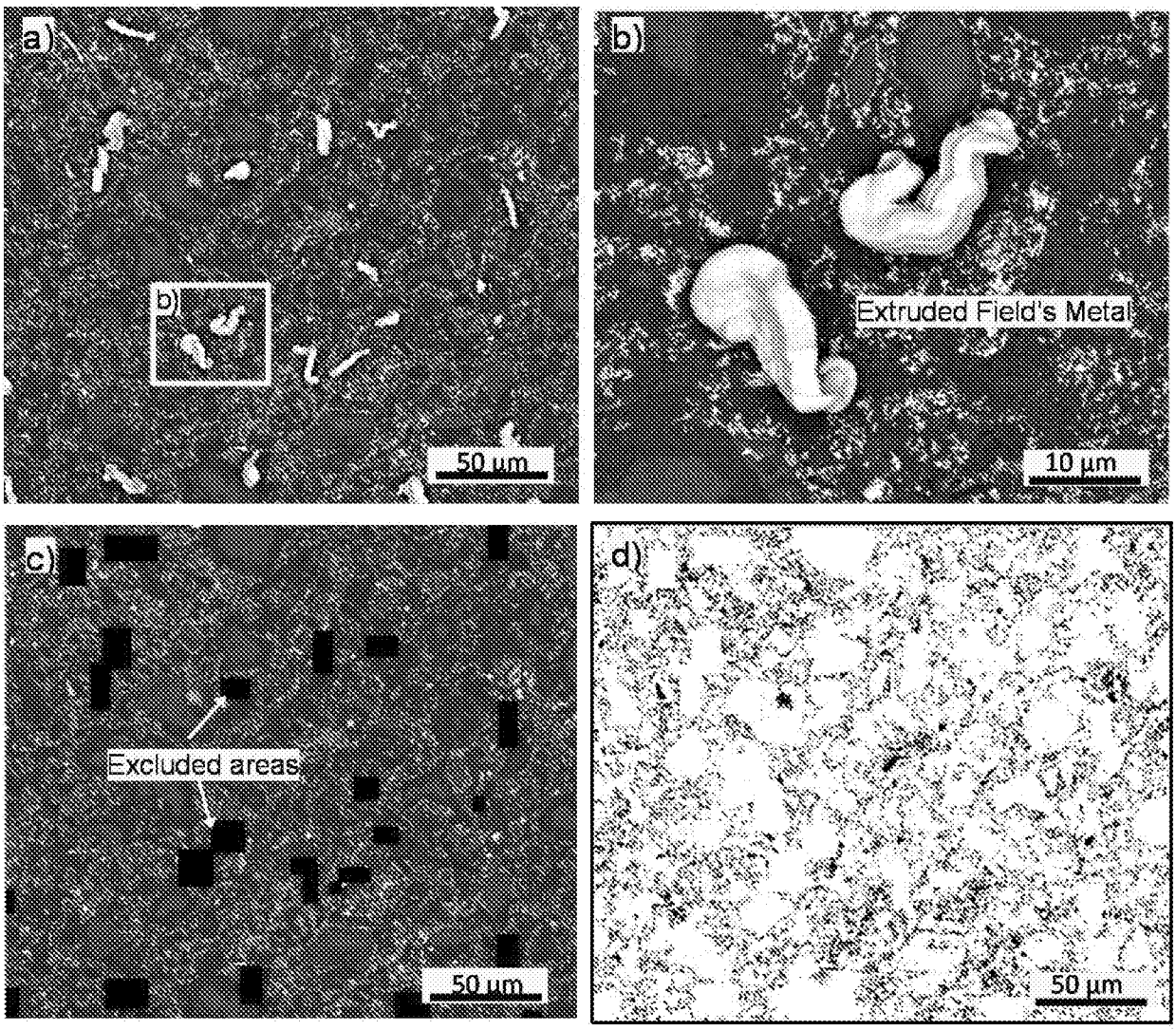

a)
b)
50 µm
b)
Extruded Field's Metal
10 µm
c)
Excluded areas
50 µm
d)
50 µm

Figure 3

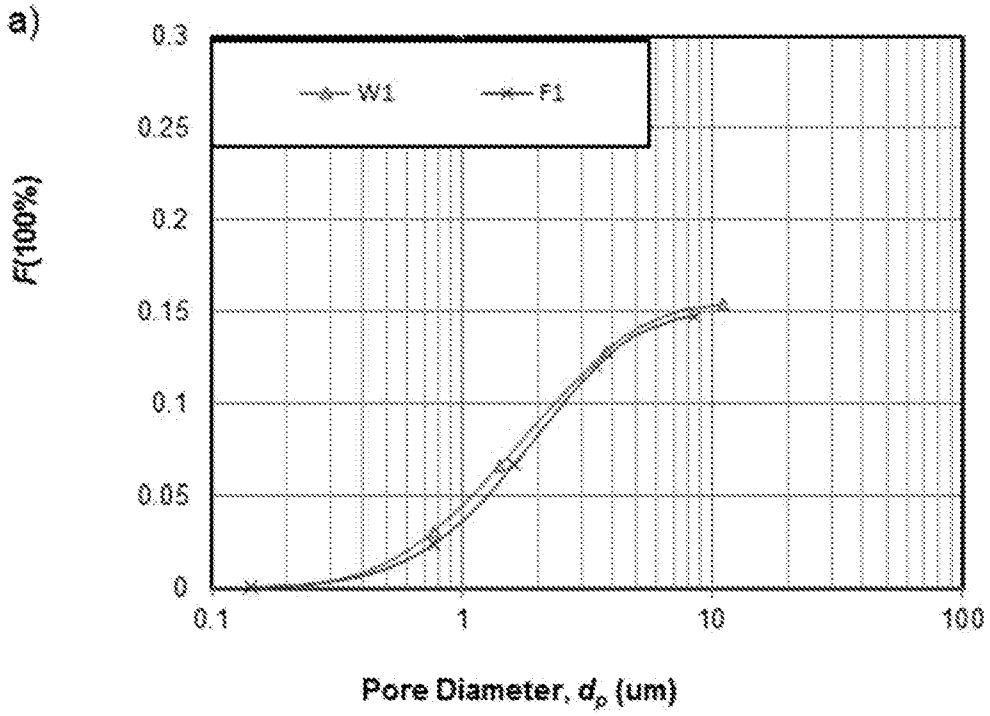


Figure 4A

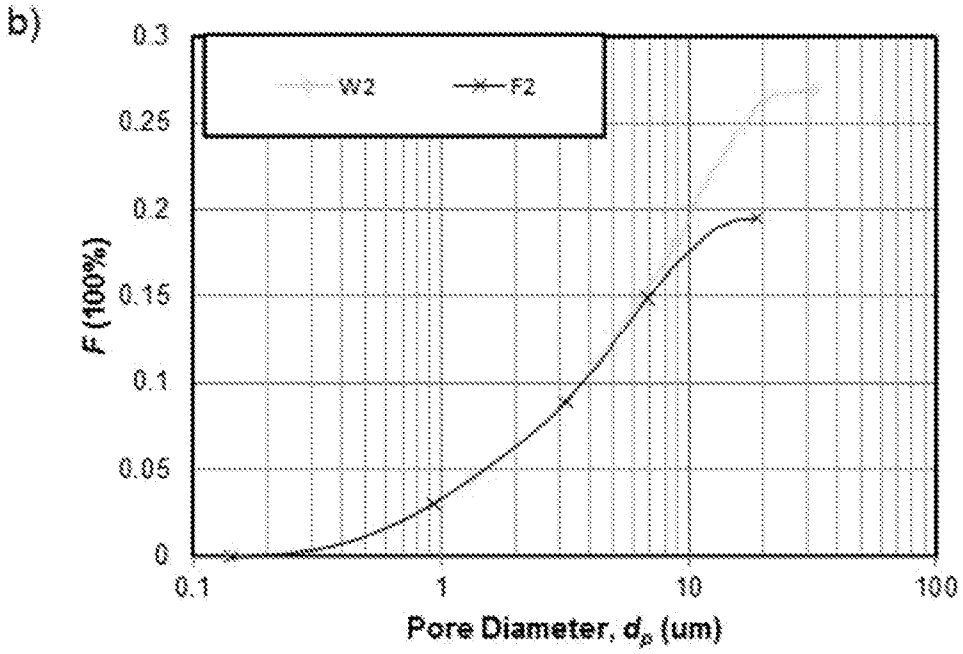


Figure 4B

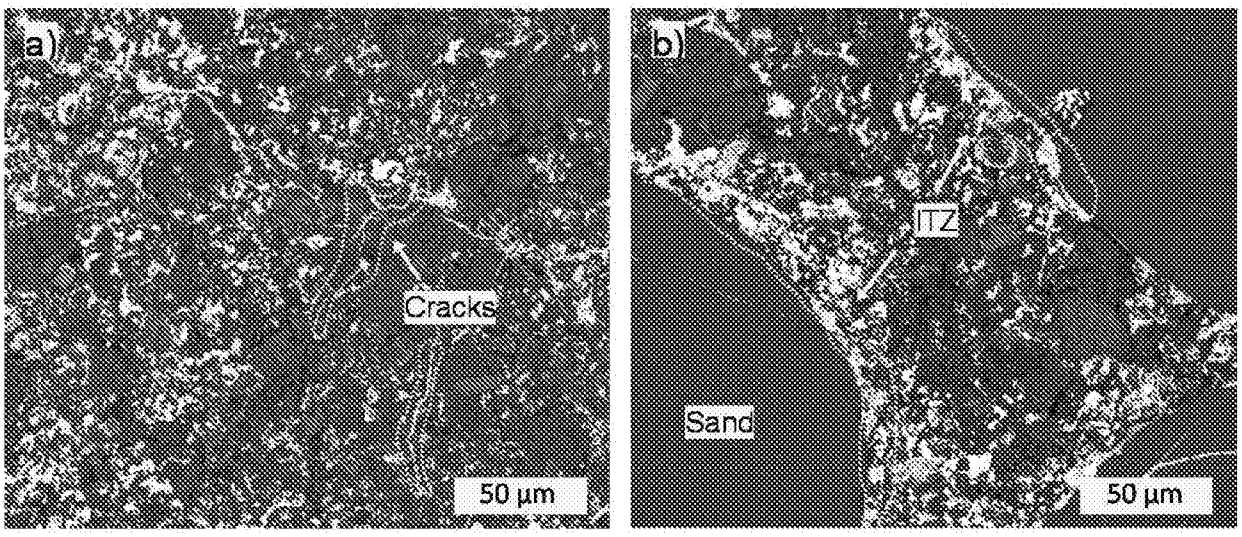


Figure 5

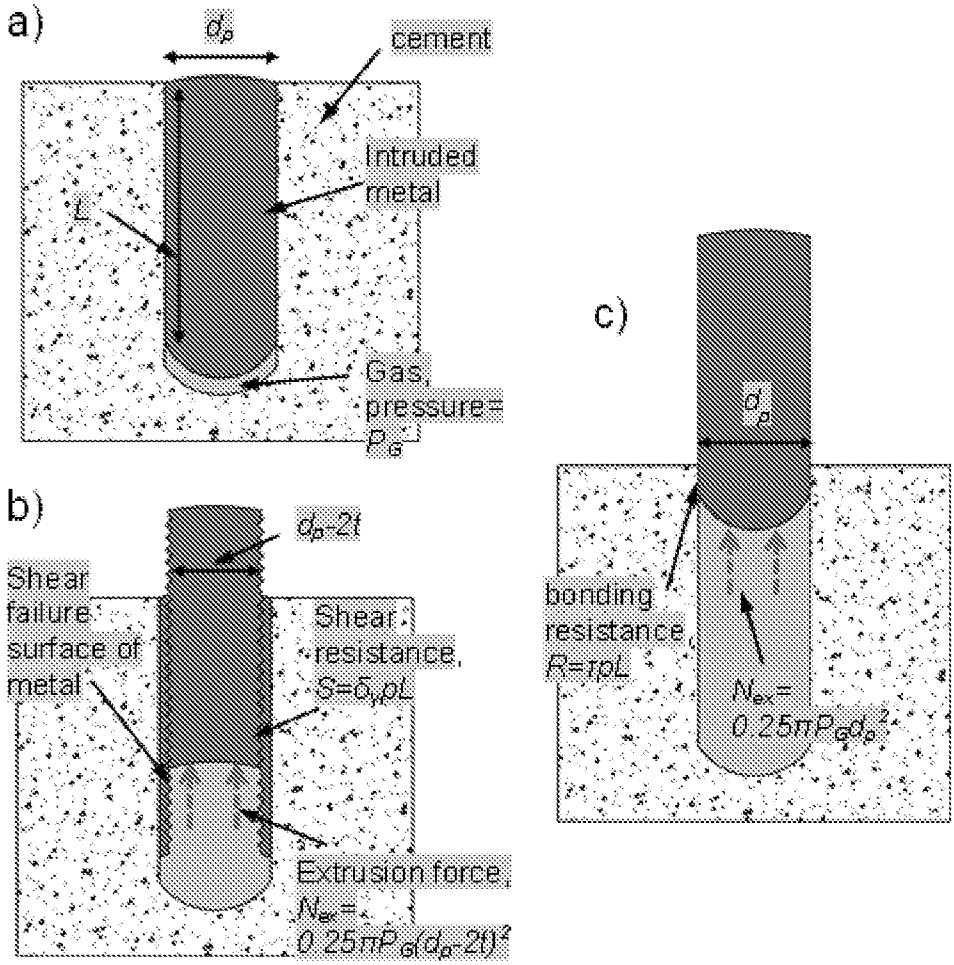

a)
d_p
cement
Intruded metal
L
Gas pressure= P_G
b)
d_p-2t
Shear failure surface of metal
Shear resistance, $S=\delta_M pL$
Extrusion force, $N_{ex}=0.25\pi P_G(d_p-2t)^2$
c)
d_p
bonding resistance, $R=\tau pL$
$N_{ex}=0.25\pi P_G d_p^2$

Figure 6

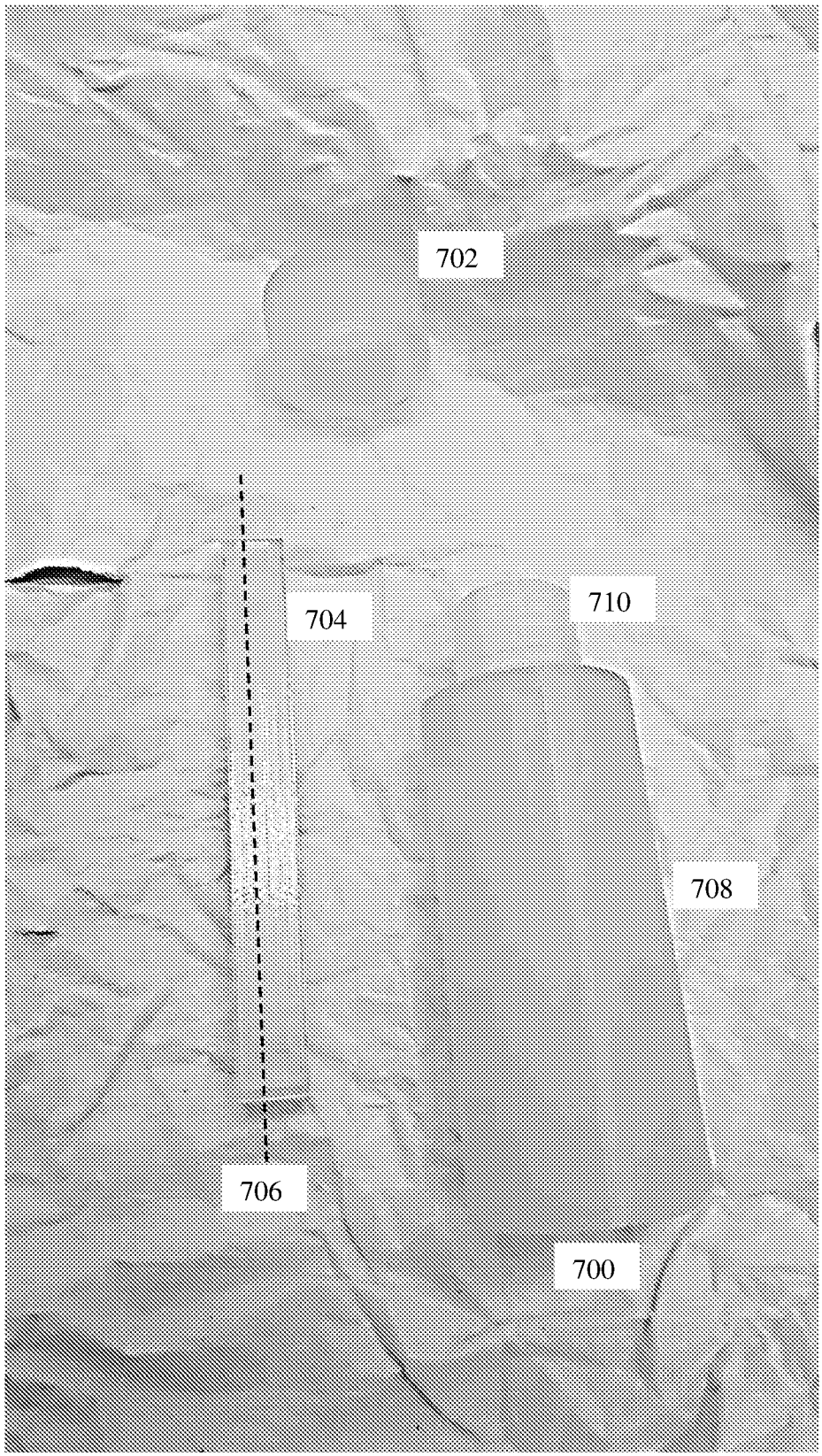


Figure 7

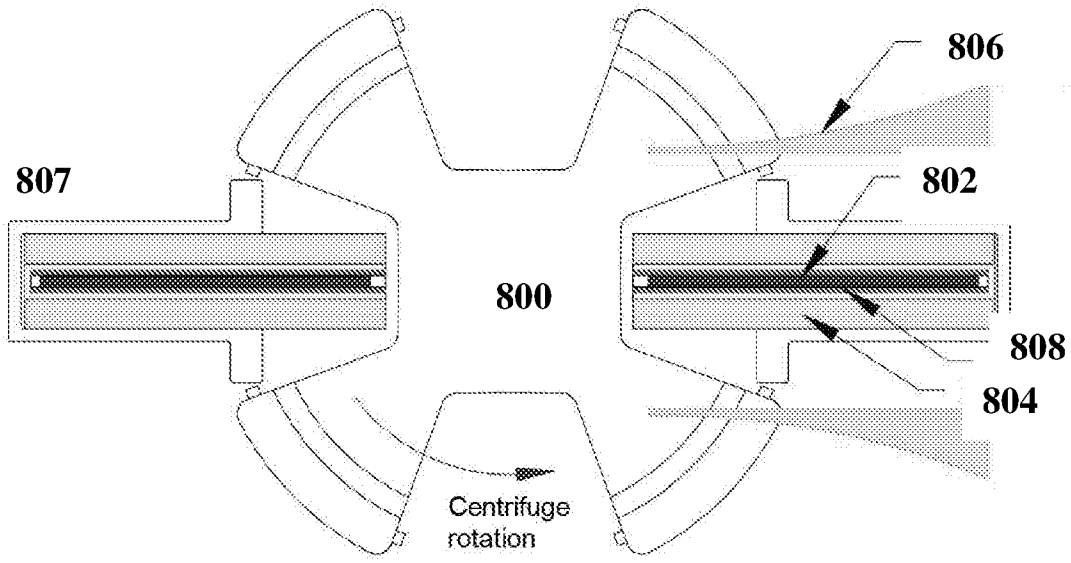


Figure 8

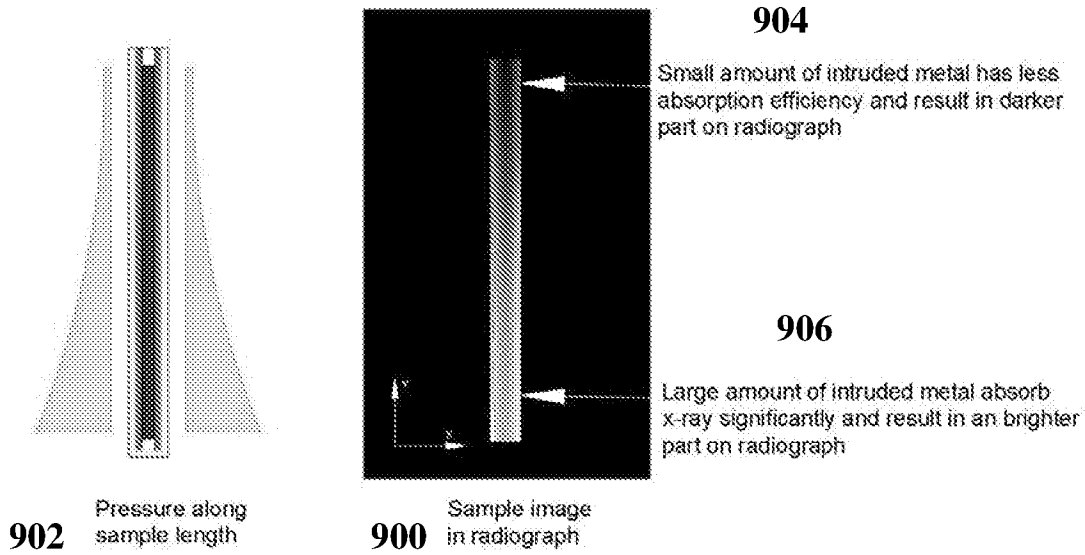


Figure 9

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU2017/050321

A. CLASSIFICATION OF SUBJECT MATTER

G01N 15/08 (2006.01) B04B 5/00 (2006.01)

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)

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)

ESPACENET, PATENW, GOOGLE: G01N15/08/C/CNO/IC AND CENTRIFUG+; ((OR (WOOD?? W METAL), (LIPOWITZ?? 2W ALLOY), CERROBEND, BENDALLOY, PEWTALLOY, MCP_158, (9UG BISMUTH, LEAD, TIN, CADMIUM), (9UG BI, PB, SN, CA), (FIELD?? W METAL), (FIELD?? W ALLOY), (9UG BISMUTH, INDIUM, TIN), (9UG BI, IN, SN), (ROSE?? W METAL), CERROSAFE, CERROLOW) AND (OR CENTRIFUG+, CENTRIPETAL B04B/LOW/IC/C/CNO)); (OR CEMENTITIOUS, CEMENT, CONCRETE, PORE?, POROSITY+, +POROUS, AGGREGATE?, SAND, (VOID? 2W FRACTION+)) AND (OR IMBIB+, FORCE, TRAP, INTRUDE, PERMEAT+, INFUS+, INTRODUC+, FORCE_IN, INTRUSION, PERMEAMETER, PERMEANT?, (INTRUD+ 2W AGENT?), PERMEABL+, ABSORB+, ADSORPTION) and similar terms. Inventor and applicant name searches.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	Documents are listed in the continuation of Box C	

[X] Further documents are listed in the continuation of Box C [X] 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	Date of mailing of the international search report
17 May 2017	17 May 2017

Name and mailing address of the ISA/AU	**Authorised officer**
AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA Email address: pct@ipaustralia.gov.au	Firoozeh Rabbani AUSTRALIAN PATENT OFFICE (ISO 9001 Quality Certified Service) Telephone No. 0262832287

INTERNATIONAL SEARCH REPORT C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		International application No. **PCT/AU2017/050321**
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	US 3,859,843 A (LOWELL) 14 January 1975	
X	Refer to the whole document and in particular to abstract, Figs. 2 & 3, col. 3 lines 12-13, col. 3 lines 39 to col. 4 line 12, col. 5 lines 1-6, col. 4 lines 51-56	1-3, 7, 9, 11-20
Y	As above	4-5, 10
	US 6,415,649 B1 (SPINLER ET AL.) 09 July 2002	
X	Refer to the whole document and in particular to abstract, Fig. 1(b)-1(d), col. 2 lines 35-61, col. 5 line 15-56, col. 7 lines 3-25	1, 6, 8, 9, 21-22
A	col. 7 line 3-7	20
	ANOVITZ, LAWRENCE M. ET AL. "Characterization and analysis of porosity and pore structures." Reviews in Mineralogy and Geochemistry, Vol. 80, No. 1, 2015, pp. 61-164	
Y	Refer to pp. 69, 122-123	4-5, 10

INTERNATIONAL SEARCH REPORT Information on patent family members	International application No. **PCT/AU2017/050321**

This Annex lists known patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document/s Cited in Search Report		**Patent Family Member/s**	
Publication Number	**Publication Date**	**Publication Number**	**Publication Date**
US 3,859,843 A	14 January 1975	US 3859843 A	14 Jan 1975
US 6,415,649 B1	09 July 2002	US 6415649 B1	09 Jul 2002
		US 6178807 B1	30 Jan 2001

End of Annex

Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.