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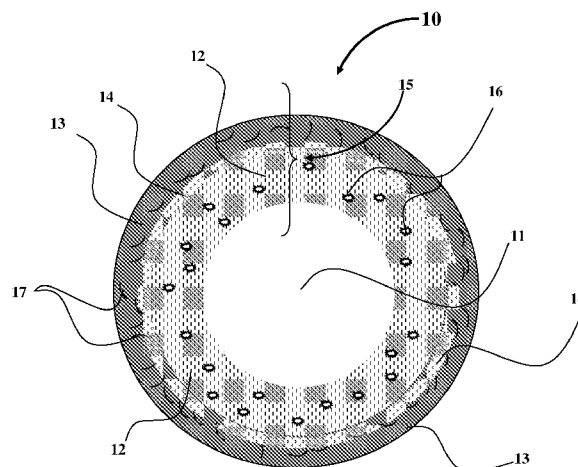


Fig. 1

(57) Abstract: A fiber-reinforced composite article useful for contaminant removal comprising at least one single layer of a fiber-reinforced composite having (a) at least one first polymer fiber-free region containing material adapted for removing contaminants, (b) at least one second polymer fiber-rich region containing fiber reinforcement material; and (c) at least one third polymer boundary region containing a portion of the first polymer fiber-free region and a portion of the second polymer fiber-rich region; a process for manufacturing the fiber-reinforced composite article; and a process for removing contaminants from a liquid fluid using the fiber-reinforced composite article.



COMPOSITE ARTICLE

FIELD

The present invention is related to a composite article useful for removing contaminants from a liquid fluid; and to a process for manufacturing the
5 composite article.

INTRODUCTION

Heretofore, various pipe structures and methods have been used for removing contaminants from liquid fluids flowing through the interior space of the pipe structures. Typically, the known methods for removing contaminants are based on
10 coatings applied to metal pipe substrates (e.g., steel, aluminum, and the like). For example,

U.S. Patent Nos. 8,726,989 and 8,746,335 disclose methods for removing contaminants from wastewater during a hydraulic fracturing process utilizing a pipe coating on the inner surface of a pipe to capture contaminants from the hydraulic fracturing operation.
15 The use of a coating applied to the inner surface of a pipe to capture contaminants has its disadvantages including, among others, the following disadvantages: (1) an extra layer is required for the overall structure of the pipe; (2) the added extra coating layer reduces the inner diameter of the pipe, thus constricting the space that fluid can flow inside the pipe; and (3) an additional processing step is required for applying the
20 coating layer to the pipe when the pipe is being manufacturing. Furthermore, the processes of the above patents do not provide for a contaminant removal mechanism which is incorporated directly into a pipe structure, that is, the pipe structure does not include an integral contaminant removal layer bonded to the pipe structure.

U.S. Patent No. 4,171,238 discloses a method of making reinforced
25 plastic composite structures. The above patent describes the incorporation of micron-size particulate, such as cement particles, for the purpose of reducing the amount of wear that occurs inside of a pipe, that is, the above patent is concerned with increasing resistance to acids or other corrosive materials. The patent further discloses an attempt to make a particulate and resin bonded together in a single matrix wherein the
30 particulate is suspended inside the resin such as a polyester resin. The above known

process disclosed in U.S. Patent No. 4,171,238 suffers from the disadvantage of requiring the distribution of particles throughout all fiber reinforced regions and the inability to preferentially place a predetermined amount of particles in a predetermined fiber reinforced region of the fiber reinforced composite to maximize functionalization while minimizing cost.

In U.S. Patent No. 6,620,475, a structure for a wound fiber reinforced plastic tubing and method for making the tubing is described. The above patent describes the formation and manufacture of a fiber-reinforced composite pipe through a filament winding process using an inner liner and one or more layers of fiber reinforcing material. The above known process disclosed in U.S. Patent No. 6,620,475 does not utilize the inner liner of the composite material as a multifunctional material that is able to capture unwanted contaminants from a flowing fluid coming in direct contact with the surface of the inner liner.

SUMMARY

Embodiments may be realized by providing a fiber-reinforced composite article useful for contaminant removal. The fiber-reinforced composite includes at least one single layer of a fiber-reinforced composite comprising several sections, areas or regions making up the single layer of the composite. For example, the composite may include the following regions in the at least one single layer: (a) at least one first polymer fiber-free region containing material adapted for removing contaminants, said contaminant removal material integrated into the first polymer fiber-free region; said first polymer fiber-free region including an inner surface and an outer surface; (b) at least one second polymer fiber-rich region containing fiber reinforcement material; said second polymer fiber-rich region including an inner surface and an outer surface; and (c) at least one third polymer boundary region containing a portion of the first polymer fiber-free region and a portion of the second polymer fiber-rich region; wherein the outer surface of the first polymer fiber-free region is integrally bonded to the inner surface of the second polymer fiber-rich region forming the at least one third polymer boundary region disposed between the first polymer fiber-free region and the second polymer fiber-rich region; wherein the third polymer boundary region further comprises a contiguous boundary of a non-delineated width between the first polymer fiber-free

region and the second polymer fiber-rich region; and wherein the first polymer fiber-free region is integrally attached to the second polymer fiber-rich region such that the first polymer fiber-free region and second polymer fiber-rich region are infused together forming the at least one third polymer boundary region.

5 Another embodiment of the present invention is directed to a process for making the above composite article. Other embodiments of the present invention include an apparatus and process of manufacturing a fiber-reinforced composite article. Still another embodiment of the present invention is directed to a process for removing contaminants using the above composite article, particularly when the composite article
10 is a conduit such as a pipe.

BRIEF DESCRIPTION OF THE DRAWINGS

For the purpose of illustrating the present invention, the drawings show a form of the present invention which is presently preferred. However, it should be understood that the present invention is not limited to the precise arrangements and
15 instrumentation shown in the drawings. In the drawings, like elements are referenced with like numerals. Therefore, the following drawings illustrate non-limiting embodiments of the present invention wherein:

Figure 1 is a schematic cross-sectional view of one embodiment of the composite article structure, shown as a pipe member, including the materials used to
20 form the layers of a composite structure of the present invention. Figure 1 includes a first polymer fiber-free region containing material adapted for removing contaminants, a second polymer fiber-rich region containing fiber reinforcement material, and a third polymer boundary region disposed in between the first polymer fiber-free region and the second polymer fiber-rich region wherein the third polymer boundary region
25 contains a portion of the first polymer fiber-free region and a portion of the second polymer fiber-rich region integrally bonded together.

Figure 2 is a micrograph (at 5x magnification) of a portion of a pipe member structure of the present invention showing a homogenous bonding region (as shown between dotted lines A and B) between the first polymer fiber-free region (as

shown between dotted lines B and C) and the second polymer fiber-rich region (as shown as numeral 22).

Figure 3 is a micrograph (at 10x magnification) of a portion of a pipe member structure of the present invention showing a homogenous bonding region (as shown between dotted lines D and E) between the first polymer fiber-free region (as shown between dotted lines E and F) and the second polymer fiber-rich region (as shown as numeral 32).

Figure 4 is a schematic cross-sectional view of another embodiment of the composite article structure, shown as a multi-layer pipe member, including the materials used to form various layers of a composite structure of the present invention. While Figure 4 shows at least five layers comprising the layered pipe member structure, the present invention composite article is not limited to a specific number of layers because the minimum number of layers required for a particular application can vary by application and operating conditions of the fabricated composite pipe. The minimum number of layers in the pipe of the present invention may be as little as one layer comprising the different regions in the cross-sectional view shown in Figure 1.

Figure 5 is a photograph showing the application of a first polymer fiber-free gel layer to a mandrel of a filament winding apparatus during the manufacturing process of the pipe structure of the present invention.

Figure 6 is a photograph showing the application of a wound second polymer fiber-rich composite over the first polymer fiber-free gel layer of Figure 5 during the manufacturing process of the pipe structure of the present invention.

DETAILED DESCRIPTION

The present invention solves several problems of the known processes. For example, the process of the present invention provides a contaminant removal mechanism which is incorporated directly into an article, such as a pipe, reducing the time required to fabricate a composite structure or part. In addition, the composite fabrication process allows for the production of an article of varying sizes such as a pipe with inner diameters of less than one inch. Furthermore, the present invention

demonstrates that functional additives can be preferentially placed in a fiber reinforced composite to maximize functionalization while minimizing cost. And, the composite structure of the present invention utilizes one or more of the composite's structural parts, such as the inner liner of a composite pipe material, as a multifunctional material
5 that is able to capture unwanted contaminants from a flowing fluid coming in direct contact with the composite surface.

In one embodiment, the present invention includes incorporating a contaminant-capturing filler into a composite material such as the incorporation of the filler results in a multi-functional composite material. The multi-functional composite
10 material provides all of the benefits of a composite article with the additional benefit of being able to capture contaminants. For example, in one preferred embodiment, the present invention is directed to a method of manufacturing a fiber-reinforced composite article for radionuclide removal. The fiber-reinforced composite material utilizes a contaminant removal process embedded within the composite material very near the
15 surface of the formed composite article which is in contact with the contaminant. The unique method of manufacture of the present invention can be utilized in a wide variety of different applications and processes for making composite articles, including for example infusion, pultrusion, filament winding, and other similar processes. In one specific embodiment, the manufacturing method of the present invention can be used
20 for manufacturing a multi-layer composite pipe article of a predetermined number of layers and of a predetermined inner diameter.

For example, in another preferred embodiment, the present invention includes the use of a filament winding method to manufacture a composite pipe structure that can be used in a piping application. However, the scope of fabrication of
25 the present invention is not limited to only a filament winding process but may include any composite fabrication method and/or polymer matrix where composite articles can be made. However, the present invention manufacturing process is more complicated than simply using a filament winding operation to fabricate a pipe. And, the present invention described herein includes a multifunctional composite material.

30 Terms used herein include the following:

“Fiber-free region” herein means a region of cured polymer matrix that that has no amount of fiber reinforcement material in the polymer matrix.

“Fiber-rich region” or “fiber-reinforced region” herein means a region of cured polymer matrix that contains an amount of fiber reinforcement material in the
5 polymer matrix.

“Contiguous boundary of a non-delineated width” herein means a qualitative interfacial region between the fiber-free region and fiber-rich region, wherein the interfacial region is of a non-measurable width and is chemically bonding the fiber-rich region and fiber-free region forming a homogeneous integral boundary
10 region generally of a cross-section where the fiber-free region and fiber-rich region are integrally in contact with one another via the boundary region.

“Radionuclide” herein means an isotope with an unstable nucleus, characterized by excess energy available to be imparted either to a newly created radiation particle within the nucleus or via internal conversion.

15 “Radionuclide removal” herein means the transfer of the unstable nucleus described above from an undesired location to a desired location.

The present invention incorporates (imbeds), for example, a radionuclide removal mechanism (e.g., in the form of BaSO₄ crystals or particles) into a fiber-reinforced composite pipe manufacturing method through the use of a two-step
20 manufacturing process (gel layer production and then filament winding) resulting in a light-weight fiber-reinforced composite pipe product adapted for contaminant capture without the need for a separate coating layer. Furthermore, the pipe with the contaminant removing layer is manufactured substantially simultaneously; and the diameter of the pipe is not limited to a specific diameter, i.e., the pipe can be made to
25 have a wide or a very narrow diameter. The capability to adjust a pipe’s diameter is advantageous because a narrow diameter pipe can be used instead of a pipe with a thick metal protective layer even for high pressure situations (for example hydraulic fracturing). By having radium capture occur on the composite pipe itself, i.e., downwell rather than above ground, this can eliminate or lessen the need for an above-
30 the-ground treatment of the water and other fluids coming out of the well.

With reference to Figure 1, there is shown a fiber-reinforced composite article, in this case a cylindrical member such as a conduit or pipe structure, generally indicated by numeral 10 with an internal space 11 of a predetermined diameter. The cylindrical pipe structure 10 of Figure 1 is prepared by integrally bonding an original first polymer fiber-free layer and an original second polymer fiber-rich layer. And, upon bonding the original first polymer fiber-free layer to the original second polymer fiber-rich layer, a single body or layer containing at least three distinct regions is formed, i.e., the overall construction of the fiber-reinforced composite article includes: (1) a first polymer fiber-free region 12; (2) a second polymer fiber-rich region 13; and (3) a third polymer boundary region 14. The above three regions 12, 13, 14 form the overall single body or layer, generally indicated by numeral 15, comprising the fiber-reinforced composite article 10 having the above three distinct regions. The boundary region 14 originates naturally as a result of curing the original first polymer fiber-free layer to the original second polymer fiber-rich layer

The fiber-reinforced composite 10, such as pipe member 10, is useful for removing contaminants present in a liquid fluid when the liquid fluid flows through the interior space 11 of the pipe member 10 and the fluid comes into contact with the first polymer fiber-free region 12 of the composite. The mechanism for removing contaminants is built into the composite structure which includes the first polymer fiber-free region 12 containing a material adapted for removing contaminants such as particles 16. The contaminant-removing particles 16 are integrated into the first polymer fiber-free region 12; and are integrally embedded in the polymer of the first polymer fiber-free region 12. The first polymer fiber-free region 12 preferably contains only particulate material 16 and no fibers 17 are contained in the fiber-free region 12.

The second polymer fiber-rich region 13 contains fiber reinforcement material 17 such continuous or discontinuous fibers 17. The fibers 17 are integrated into the second polymer fiber-rich region 13; and are integrally embedded in the polymer of the second polymer fiber-rich region 13. The second polymer fiber-rich region 13 preferably contains only fibers 17 and no particles 16 are contained in the fiber-rich region 13.

As aforementioned, upon bonding the outer surface of the first polymer fiber-free region and the inner surface of the second polymer fiber-rich region, a third polymer boundary region 14 is formed. The outer surface of the first polymer fiber-free region 12 is integrally bonded to the inner surface of the second polymer fiber-rich region 13 forming the third polymer boundary region 14 disposed between the first polymer fiber-free region 12 and the second polymer fiber-rich region 13 as shown in Figure 1. As a result of bonding, the third polymer boundary region 14 contains a portion of the first polymer fiber-free region 12 having the particles 16 and a portion of the second polymer fiber-rich region 13 having the fibers 17. By its nature, the third polymer boundary region 14 comprises a contiguous boundary of a non-delineated width and a non-delineated boundary line between the first polymer fiber-free region 12 and the second polymer fiber-rich region 13; that is, the first polymer fiber-free region is integrally attached to the second polymer fiber-rich region such that the first polymer fiber-free region and second polymer fiber-rich region are infused together forming the third polymer boundary region 14 comprising a polymer matrix infused with some fibers and some contaminant-capturing particles intermingled with each other.

In Figure 2, there is shown a micrograph at 5x magnification of part of the pipe structure of Figure 1, generally indicated by numeral 20, including a first polymer fiber-free region 21 integrally bonded to a second polymer fiber-rich region 22 forming a third polymer boundary region 23 disposed somewhere between the dotted lines labeled A and B; and between the first polymer fiber-free region 21 and the second polymer fiber-rich region 22.

In Figure 3, there is shown a micrograph at 10x magnification of part of the pipe structure of Figure 1, generally indicated by numeral 30, including a first polymer fiber-free region 31 integrally bonded to a second polymer fiber-rich region 32 forming a third polymer boundary region 33 disposed somewhere between the dotted lines labeled D and E; and between the first polymer fiber-free region 31 and the second polymer fiber-rich region 32. The inner surface of the first polymer fiber-free region 31 forms the outer perimeter of internal space 34 (shown as dotted line F) of a pipe. In Figure 3 again, there is shown the particles 35 embedded in the first polymer

fiber-free region 31; and the fibers 36 embedded in the second polymer fiber-rich region 32.

With reference to Figure 1 again, there is shown a composite structure 10, such as a pipe structure 10 and the inner space of the pipe structure is indicated by numeral 11. The diameter of the space 11 can be, but is not limited to, generally from about 3 mm to about 300 mm in one embodiment, from about 6 mm to about 250 mm in another embodiment, and from about 10 mm to about 200 mm in still another embodiment. The diameter of the space 11 can vary depending on the application in which the pipe will be used. For example, piping used for a hydraulic fracturing process is generally in the range of from about 20 mm to about 200 mm in diameter.

Another embodiment of a composite pipe structure is shown in Figure 4. The composite pipe structure, generally indicated by numeral 40, includes a multi-layer construction including optional additional layers and/or optional regions. For example, the pipe 40 may include a first polymer fiber-free gel layer 41 containing a particulate material for removing contaminants 47 such as barium sulfate, an outside second polymer fiber-rich composite layer 42 containing fibers 48, a glass veil 43, and a release film or layer 44, all disposed on the outer surface of an inner mandrel 45 (e.g., made of HDPE) with internal space 46. Any number of other optional layers can be added to the composite structure 40 depending on the enduse of the final composite pipe product.

With reference to Figure 4 again, the first polymer fiber-free gel layer 41 of the composite article 40 may be made of any conventional curable polymer resins including for example bisphenol-A-based resins, bisphenol-F-based resins, and other known epoxides and curable (thermosetting) resins; and mixtures thereof. The gel layer 41 may also include other additives such as monofunctional reactive diluents (including for example cresyl glycidyl ether, butyl glycidyl ether, and the like), difunctional reactive diluents (including for example butanediol diglycidyl ether, butane dioxide, and the like), non-reactive diluents (including for example dibutyl phthalate and phenolic compounds and the like), fillers (including for example carbon black, titanium dioxide, and the like), and mixtures thereof.

Additionally, a curing agent is used in the first polymer fiber-free gel layer 41 to react with the first polymer to form the cross-linked first polymer network. The curing agent (also known as a hardener or crosslinking agent) may include for example polyamides, polyamidoamines, phenols, amino-formaldehydes, carboxylic acid functional polyesters, anhydrides, polysulfides, polymercaptans, and mixtures thereof.

The first polymer fiber-free gel layer 41 also includes particulate material for removing contaminants such as barium sulfate particulate 47 dispersed in the first polymer fiber-free gel layer 41. Other particles 47 that can be dispersed and embedded in the first polymer fiber-free gel layer 41 may include for example barium sulfate particles with a diameter of from about 1 μm to about 5 μm .

The amount of particles 47 present in the first polymer fiber-free gel layer 41 may be generally from about 10 % by weight to about 95 % by weight in one embodiment, from about 20 % by weight to about 90 % by weight in another embodiment, and from about 30 % by weight to about 85 % by weight in still another embodiment.

In one preferred embodiment, the first polymer fiber-free gel layer 41 may include a bisphenol-A-based epoxy resin as the first polymer, an amine curing agent, and barium sulfate particulate.

One of the beneficial properties of the gel layer 41 is the capability of the gel layer 41 to remove contaminants such as radionuclide from a liquid fluid coming into contact with the gel layer 41. "Fiber-free" with reference to the amount of fibers 48 present in the gel layer 41 means there is less than 15 % by weight amount of fibers in the gel layer 41 and preferably zero.

The first system or formulation for making the first polymer fiber-free gel layer 41, is designed to have an initial viscosity of at least 20,000 mPa-s to prevent sagging and dripping when the gel layer 41 is applied to the mandrel 45; and the formulation is designed to have a gel time of approximately (~) 20 minutes. For example the gel layer 41 may have an initial viscosity of generally from about 10,000 mPa-s to about 40,000 mPa-s in one embodiment, from about 15,000 mPa-s to about

30,000 mPa-s in another embodiment, and from about 18,500 mPa-s to about 25,000 mPa-s in still another embodiment. For example the gel layer 41 may have a gel time of generally from about 5 minutes (min) to about 45 min in one embodiment, from about 10 min to about 30 min in another embodiment, and from about 15 min to about 25 min in still another embodiment.

The thickness of the gel layer 41 of the composite article structure 40 can be generally from about 0.25 millimeters (mm) to about 5 mm in one embodiment, from about 0.5 mm to about 3 mm in another embodiment, and from about 1 mm to about 2 mm in still another embodiment. A gel layer 41 that is too thin (i.e., less than about 0.25 mm) may not provide enough coverage to the inside of a pipe member and will result in an underperforming part with less contaminant capture than desired. A gel layer 41 that is too thick (i.e., greater than about 0.5 mm) can result in adverse processing issues such as gel-layer dripping and waste.

In the embodiment shown in Figure 1, the gel layer 12 is bonded to the composite layer 13 forming a bonding region 14. In a preferred embodiment, shown in Figure 4, the gel layer 41 of the composite article structure 40 of the present invention is disposed in between a veil layer 43 and a release layer 44; and the second polymer fiber-rich composite layer 42 is disposed on the outer surface of the veil layer 43.

As shown in Figure 4, outer surface of the gel layer 41 is disposed in contact with and adjacent to the inner surface of the glass veil layer 43; and the inner surface of the gel layer 41 is disposed in contact with and adjacent to the outer surface of a release layer 44. The release layer 44, with the inner surface of the release film or layer 44 disposed on the outer surface of the mandrel 45, is used to avoid the composite pipe structure from sticking to the mandrel 45.

The second polymer fiber-rich composite layer 42 of the composite article 40, shown in Figure 4, may be made of any of the conventional polymer resins described above with reference to the first polymer fiber-free composite layer 41. The polymer resin used to manufacture the second polymer fiber-rich composite layer 42 can be the same or different than the polymer resin used to manufacture the first polymer fiber-free composite layer 41.

Additionally, a curing agent is used in the second polymer fiber-rich composite layer 42 to react with the second polymer to form the cross-linked second polymer network.

5 The second polymer fiber-rich composite layer 42 also includes a fiber-reinforcement which can be for example continuous fiber or discontinuous fiber. The fibers 48 in the polymer matrix of the composite layer 42 may be of different origins, including but not limited to, carbon fibers (including for example pitch based and polyacrylonitrile based), glass fibers (including for example e-glass, s-glass, and the like), aramid fibers, natural fibers, and mixtures thereof. The fibers can be applied in
10 any direction in a three-dimensional coordinate frame that is consistent with theory dictating a functioning laminate structure.

The amount of fibers 48 present in the second polymer fiber-rich composite layer 42 may be generally from about 50 % by weight to about 85 % by weight in one embodiment, from about 60 % by weight to about 80 % by weight in
15 another embodiment, and from about 65 % by weight to about 70 % by weight in still another embodiment.

The thermosetting or thermoplastic resin used as the second polymer matrix of the composite layer 42 preferably has a suitable viscosity to achieve homogenous fiber bundle impregnation during a specified residence time dictated by
20 the particular individual process used (for example, in a filament winding process, the residence time is the time the fiber bundle spends in the impregnation bath). For example, in a preferred embodiment, the composite layer 42 may be made of continuous fiber rovings and a thermosetting resin matrix such as an epoxy resin. Alternatively, the composite layer 42 may comprise a continuous fiber roving and a
25 thermoplastic matrix. The thermoplastic matrix can be for example polypropylene, polysulfone, polyether ether ketone and the like; and mixtures thereof.

One of the beneficial properties of the composite layer 42 is that the layer 42 is free of the radionuclide capturing particle material 47 and exhibits a homogenous laminate structure (i.e., the composite layer 42 is free of defects, for
30 example less than about 5 % by weight [defects]). “Free of particles” with reference to

the amount of particles 47 in the composite layer 42 means there is less than 10 % by weight amount of particles in the composite layer 42 and preferably zero.

In one embodiment, the composite layer 42 of the composite article structure 40 of the present invention is disposed on the outer surface of the veil layer 43. As shown in Figure 4, the layer 42 is disposed in contact with and adjacent to the outside surface of the veil layer 43. For example, the composite layer 42 may be laid on the top surface of the veil layer 43 and then all of the layers of the article 40 can be chemically bonded into the polymer matrix together during the curing process.

The thickness of the composite layer 42 of the composite article structure 40 is not limited to a predetermined thickness. However, the thickness of the composite layer 42 can be generally from about 0.25 mm to about 100 mm in one embodiment, from about 1 mm to about 60 mm in another embodiment, and from about 5 mm to about 40 in still another embodiment.

The veil layer 43 of the composite article 40, shown in Figure 4, may be made of various materials including for example glass, polyester, carbon, or mixtures thereof. For example, in a preferred embodiment, the veil layer 43 may be made of e-glass.

One of the beneficial properties of the veil layer 43 is to provide a separating layer such that a more defined boundary can be establish between the first polymer fiber-free region containing a radionuclide removal mechanism and the second polymer fiber-rich region containing fiber reinforcement which provides mechanical strength to article 40.

In one embodiment, the veil layer 43 of the composite article structure 40 of the present invention is laid in between the composite layer 42 and the gel layer 41. As shown in Figure 4 the veil layer 12 is disposed in contact with and adjacent to the inner surface of the composite layer 42; and in contact with and adjacent to the outer surface of the gel layer 41.

The thickness of the veil layer 43 of the composite article structure 10 can be generally from about 8 μ m to about 100 μ m in one embodiment, from about 10

μm to about 75 μm in another embodiment, and from about 15 μm to about 50 μm in still another embodiment.

The release film layer 44 of the composite article 40, shown in Figure 4, may be made of any material that is suitable for providing an advantageous release
5 mechanism for releasing the composite article 40 from the mandrel 45. In a preferred embodiment for example, the release film layer 44 may be made of paste waxes, liquid polymers, polyvinyl alcohols (PVA's) or semi-permanents.

In one embodiment, the release film layer 44 of the composite article structure 40 of the present invention is disposed in between the gel layer 41 and the
10 inner mandrel 45. As shown in Figure 4, the release film layer 44 is disposed in contact with and adjacent to the inner surface of the gel layer 41; and the release film layer 44 is disposed in contact with and adjacent to the outer surface of the mandrel 45.

The thickness of the release film layer 44 of the composite article structure 40 can be generally from about 0.01 mm to about 2 mm in one embodiment,
15 from about 0.05 mm to about 1 mm in another embodiment, and from about 0.1 mm to about 0.5 mm in still another embodiment.

The inner mandrel 45, shown in Figure 4, may be made of for example any conventional material with properties adapted to withstand the operating and curing conditions of the process of the present invention. For example, the inner mandrel 45
20 may be made of stainless steel, carbon steel, aluminum, iron and thermoplastics (including for example polyether ether ketone, high-density polyethylene, and the like).

As shown in Figure 4, the outer surface of the mandrel 45 useful in the present invention is disposed in contact with and adjacent to the inner surface of the release film layer 44. The mandrel 45 only needs to be thick enough to support applied
25 layers throughout the processing of the composite article 40. Depending on the material used, the thickness of the mandrel 45 can vary. Other considerations for the thickness of the mandrel 45 can include processing speed, curing temperatures, and type of resins used in the process. For example, the thickness of the inner mandrel 45 of the composite article structure 40 can be generally from about 3 mm to about 300

mm in one embodiment, from about 6 mm to about 250 mm in another embodiment, and from about 10 mm to about 200 mm in still another embodiment.

The structure 40 of Figure 4 is shown with a number of layers to form a multi-layer construction. However, the number of layers for the structure 40 is not limited to the layers as shown in Figure 4. Any number of layers can make up the overall multi-layer structure 40. For example the number of layers can be generally from about 2 layers to about 15 layers in one embodiment, from about 3 layers to about 10 layers in another embodiment, and from about 4 layers to about 8 layers in still another embodiment. In a preferred embodiment, the minimum number of layers that can be used to manufacture the composite structure 40 can be for example three layers: (1) a first polymer fiber-free gel layer, (2) a veil layer, and (3) a second polymer fiber-rich layer.

The overall diameter of the pipe structure 40 with the multi-layer construction as shown in Figure 4 can also vary depending on the application in which the pipe structure 40 will be used. However, the overall diameter of structure 40 can be generally from about 5 mm to about 400 mm in one embodiment, from about 20 mm to about 300 mm in another embodiment, and from about 30 mm to about 200 mm in still another embodiment.

The composite product or article, such as a pipe, prepared by the process of the present invention exhibits unexpected and unique properties. In one embodiment for example, the overall fabricated composite article can weigh less than a similar conventional metal part performing the same function. For example, the composite of the present invention can weigh less than a metal counterpart part generally less than about 5 % to about 75 % in one embodiment, less than about 10 % to about 60 % in another embodiment, and less than about 15 % to about 50 % in still another embodiment.

Another broad scope of the present invention includes a process for manufacturing a fiber-reinforced composite article for radionuclide removal. The process includes manufacturing a composite article by bonding at least two polymer layers to form a single composite article containing at least one first polymer fiber-free region, at least a second polymer fiber-rich region, and a third boundary region

disposed between (separating) the first polymer fiber-free region and the second polymer fiber-rich region. The system, composition, or formulation, includes components to manufacture: (a) a first polymer fiber-free region containing contaminant-removing particles such as radionuclide removal particles; and
5 components to manufacture: (b) a second polymer fiber-rich region containing fiber reinforcement material.

The fiber-free polymer region containing a contaminant-capturing material such as radionuclide-removal particles comprises the gel layer of the composite. The composition used to form the gel layer of the composite includes for
10 example, the following compounds or components: (i) an epoxy resin such as a novolac type epoxy resin, (ii) a curing agent such as an amine curing agent for curing the epoxy resin, and (iii) a contaminant-capturing particulate material such as BaSO₄. The above gel layer composition can also include (iv) a dispersing aid (e.g., BYK-940) for
homogenously dispersing the above components throughout the fiber-free polymer
15 region, particularly for dispersing the above particulate material into the fiber-free polymer region.

In one embodiment, the first formulation is applied as a gel layer and is designed to have a high (e.g., > than about 20,000 mPa-s) initial viscosity, to prevent sagging and dripping, and to have a fast gel time (e.g., < 1 hour at 25°C). For example,
20 the viscosity of the first formulation to form the gel layer can generally be from about 20,000 mPa-s to about 80,000 mPa-s in one embodiment, from about 30,000 mPa-s to about 60,000 mPa-s in another embodiment, and from about 40,000 mPa-s to about 55,000 mPa-s in still another embodiment. If the viscosity of the gel layer resin
formulation is less than the described viscosities the gel layer will have a tendency to
25 sag or drip off the mandrel used in the winding process and may lead to inhomogeneous distribution of the contaminant removal mechanism in the inner layer of the composite pipe. If the viscosity of the gel layer resin formulation is greater than the described viscosities then the mixed formulation may be too viscous to apply and may lead to inhomogeneous distribution of the contaminant removal mechanism in the
30 inner layer of the composite pipe.

For example, the gel time of the first resin formulation can generally be from about 2 minutes to about 50 minutes in one embodiment, from about 3 minutes to about 30 minutes in another embodiment, and from about 5 minutes to about 20 minutes in still another embodiment. If the gel time of the resin formulation is too short, then the application of the gel layer will become very difficult and adequate bonding may not be achieved between the fiber-free region and fiber-rich region.

The epoxy resin used to form the gel layer can include, for example, a bisphenol-A-based resin, a bisphenol-F-based resin, other thermosetting resins, and mixtures thereof. The formulation for forming the gel layer may also contain other optional compounds such as a monofunctional reactive diluent (including for example, cresyl glycidyl ether, butyl glycidyl ether, and the like.), a di-functional reactive diluent (including for example butanediol diglycidyl ether, butane dioxide, and the like.), a non-reactive diluent (including for example dibutyl phthalate and phenolic compounds), a filler (including for example carbon black, titanium dioxide, and the like.); and mixtures thereof.

In a preferred embodiment, the epoxy useful in the process of the present invention may include for example, one or more bisphenol-A-based resins, bisphenol-F-based resins, and mixtures thereof.

One of the beneficial properties of the epoxy resin used in the present invention is its initial viscosity as specified in the ranges described above so that dripping of the mixed resin formulation off the mandrel does not occur.

The curing agent used to cure the epoxy resin present in the gel layer can include, for example, an amine, a polyamide, a polyamidoamine, a phenol, an amino-formaldehyde, a carboxylic acid functional polyester, an anhydride, a polysulfide, a polymercaptan; and mixtures thereof.

In a preferred embodiment, the curing agent useful in the process of the present invention may include for example, one or more aliphatic amines, cycloaliphatic amines, polyetheramines, and mixtures thereof.

One of the beneficial properties of the curing agent is a low equivalent hydrogen weight (no greater than 60 amine hydrogen equivalent weight [AHEW]) so that only a small amount of the amine curing agent is needed. A high hydrogen equivalent weight will need a large amount of curing agent and will decrease the
5 viscosity of the gel-layer so that it is un-usable.

The particulate material added to the gel layer can include, for example, any particulate in a micro or nanoscale size that is advantageous for capturing contaminants and removing the contaminants from a contaminated liquid fluid such as radionuclides where the particulate and contaminant come into direct contact with one
10 another in the fiber-free region containing contaminant-capturing particles. For example, the contaminant-capturing particulate material may include barium sulfate (BaSO_4).

The contaminant-capturing particulate used in the present invention may include, for example, metal-sulfates, metal oxides, and/or any combination thereof.
15 The contaminant-capturing particles are solid at room temperature. The contaminant-capturing particulate may have a melting point greater than 500 °C, greater than 800 °C, and/or greater than 1000 °C. The melting point of the contaminant-capturing particulate may be less than 2500 °C. Exemplary metal-sulfates include alkali metal-sulfates and alkaline earth metal-sulfates. Exemplary metal-sulfates include barium
20 sulfate, strontium sulfate, and mixtures thereof. In one preferred embodiment, the contaminant-capturing particulate is barium sulfate. Exemplary metal oxides include manganese oxides such as manganese(II) oxide (MnO), manganese(II,III) oxide (Mn_3O_4), manganese(III) oxide (Mn_2O_3), manganese dioxide (MnO_2), and manganese(VII) oxide (Mn_2O_7). Exemplary manganese oxide based minerals include
25 birnessite, hausmannite, manganite, manganosite, psilomelane, and pyrolusite.

The contaminated liquid that is processed using a fiber-reinforced composite article of the present invention may include, for example water, brine, a blend of crude oil and water, or a blend of crude oil and brine.

In a preferred embodiment, the particulate material useful in the process
30 of the present invention may include for example, one or more forms, shapes or sizes of barium sulfate (BaSO_4). One of the beneficial properties of the particulate material

includes the capability of the particulate material to capture and entrap a radionuclide by the radionuclide coming into direct contact with the particulate material.

The concentration of the particulate material used in the present invention may range generally from about 5 wt % to about 90 wt % in one
5 embodiment, from about 15 wt % to about 85 wt % in another embodiment, and from about 25 wt % to about 80 wt % in still another embodiment. If there is too little particulate material in the gel layer, there may not be sufficient material to capture the contaminant of interest. If there is too much particulate material in the gel layer, inter-layer and intra-layer
10 bonding may not be sufficient to form a homogenous article.

The dispersing aid added to the gel layer can include, for example, any additive that decreases settling of additives for contaminant removal. In a preferred embodiment, the dispersing aid useful in the process of the present invention may include for example, one or more polysiloxane copolymer that decreases settling of
15 inorganic additive for radionuclide removal.

One of the beneficial properties of the dispersing aid is its ability to keep the particle for radionuclide removal from settling in the gel-layer.

The concentration of the dispersing aid used in the present invention may range generally from about 0 wt % to about 2 wt % in one embodiment, from
20 about 0.25 wt % to about 1.5 wt % in another embodiment, and from about 0.5 wt % to about 1 wt % in still another embodiment. The use of too little dispersing aid will lead to inefficiently dispersed particles. The use of too much dispersing aid will affect the performance of the contaminant removal mechanism.

25 Optional additives that can be added to the formulation for forming the gel layer may include for example monofunctional reactive diluents (including for example cresyl glycidyl ether, butyl glycidyl ether, and the like.), di-functional reactive diluents (including for example butanediol diglycidyl ether, butane dioxide, and the like), non-reactive diluents (including for example dibutyl phthalate and phenolic
30 compounds) useful for modifying the viscosity of the gel layer such that

advantageously the gel layer can be processed through the process of the present invention.

The concentration of the optional additives used in the present invention may range generally from 0 wt % to about 5 wt % in one embodiment, from about 0.1
5 wt % to about 3 wt % in another embodiment, and from about 0.5 wt % to about 1 wt % in still another embodiment. If too much viscosity modifier is used (e.g., > 5 wt %), the mechanical properties of the formulation may be adversely impacted.

In one embodiment, an accelerator may be used as an optional additive that can be added to form the gel layer. For example, a gel or cure accelerator useful
10 for accelerating the rate of crosslinking within the curing formulation may be used.

The concentration of the optional accelerator used in the present invention may range generally from 0 wt % to about 3 wt % in one embodiment, from about 0.1 wt % to about 2 wt % in another embodiment, and from about 0.5 wt % to about 1 wt % in still another embodiment. If too much gel or cure accelerator is added
15 to the gel layer formulation, then the formulation may be too reactive and a homogenous gel layer may not be achieved.

Another optional additive that can be added to form the gel layer may include for example fillers (including for example carbon black, titanium dioxide, and the like) useful for providing advantageous properties that the gel layer could not
20 achieve without such as a thermal barrier, wear reduction barrier and the like.

The concentration of the filler used in the present invention may range generally from 0 wt % to about 25 wt % in one embodiment, from about 0.1 wt % to about 15 wt % in another embodiment, more preferably from about 0.5 wt % to about 10 wt % in still another embodiment. If too much filler beyond the above
25 concentrations is added to the formulation, then the formulation may be too reactive and a homogenous gel-layer may not be achieved. If too little filler outside the ranges above is used, than the desired properties achieved through incorporation of the filler may not be achieved.

The second polymer fiber-rich or fiber-reinforced region of the
30 composite is formed using a composition, system or formulation containing the

following compounds or components: (i) a polymer resin, (ii) a curing agent for curing the resin, and (iii) a fiber reinforcement material.

The second formulation which can be used in the present invention may include a conventional formulation for filament winding with low viscosity (for example, from about 350 mPa-s to about 600 mPa-s) for homogenous fiber bundle impregnation and long gel times (for example, > 6 hours at 25 °C). For example, the viscosity of the second formulation can generally be from about 200 mPa-s to about 1000 mPa-s in one embodiment, from about 300 mPa-s to about 800 mPa-s in another embodiment, and from about 350 mPa-s to about 600 mPa-s in still another embodiment. The viscosity of the formulation needs to be in accordance with a traditional filament winding system. Too high a viscosity will result in poor fiber bundle impregnation. Too low a viscosity will result in resin drainage from the fiber bundle.

It is desired to achieve homogenous fiber bundle impregnation such that the resulting structure will perform as designed without any deleterious amount of wet out of the resin formulation as can be determined by techniques known in the art. For example, the gel time of the second formulation can generally be from about 1 hour (hr) to about 16 hr in one embodiment, from about 2 hr to about 12 hr in another embodiment, and from about 4 hr to about 8 hr in still another embodiment. If the gel time is too short, the entire composite structure may not be formed before the curing reaction occurs, leading to a heterogeneous laminate structure. There are no major consequences to having too long a gel time beyond the 16 hours discussed about other than the process would be uneconomical and inefficient.

The polymer resin used to form the fiber-rich (fiber-reinforced) layer can include, for example, a bisphenol-A-based resin, a bisphenol-F-based resin, a monofunctional reactive diluent (including for example, cresyl glycidyl ether, butyl glycidyl ether, and the like.), di-functional reactive diluents (including for example, butanediol diglycidyl ether, butane dioxide, and the like.), non-reactive diluents (including for example, dibutyl phthalate and phenolic compounds), fillers (including for example, carbon black, titanium dioxide, and the like.), and mixtures thereof.

Additionally, a curing agent is used to form the cross-linked polymer network that may be comprised of polyamides, polyamidoamines, phenol and amino-formaldehydes, carboxylic acid functional polyesters, anhydrides and polysulfides and polymercaptans; and mixtures thereof.

5 In a preferred embodiment, the polymer resin useful in the process of the present invention may include for example, one or more bisphenol-A-based resins, one or more di-functional reactive diluents, and mixtures thereof.

 One of the beneficial properties of the polymer resin of the second formulation is its low initial viscosity, (i.e., the formulation which includes the resin,
10 additives, fillers and curing agent). For example, the initial viscosity of the formulation can be from about 350 mPa-s to about 600 mPa-s.

 The concentration of the polymer resin used in the present invention may range generally from about 60 wt % to about 99 wt % in one embodiment, from about
15 70 wt % to about 90 wt % in another embodiment, and from about 80 wt % to about 85 wt % in still another embodiment. Use of too much reactive diluent (and therefore reducing the amount of epoxy resin in the overall formulation to below 60 wt %) will significantly and adversely impact the thermal and mechanical properties of the final cured composite article.

20 The curing agent used to cure the polymer resin present to form the fiber-reinforced polymer region can include, for example, any of the curing agents described above with reference to the gel layer. For example, the curing agent can be an amine, a polyamide, a polyamidoamine, a phenol, an amino-formaldehyde, a carboxylic acid functional polyester, an anhydride, a polysulfide, a polymercaptan; and
25 mixtures thereof.

 In a preferred embodiment, the curing agent useful in the process of the present invention may include for example, one or more aliphatic amines, cycloaliphatic amines, polyetheramines, and mixtures thereof.

 The reinforcement material used to form the fiber-rich region layer can
30 include, for example, discontinuous or continuous glass fibers (e.g., e-glass, s-glass,

and the like), carbon fibers (e.g., polyacrylonitrile [PAN] fibers and pitch based fibers), aramid fibers, natural fibers, and mixtures thereof.

In a preferred embodiment, the reinforcement material useful in the process of the present invention may include for example, one or more continuous or
5 discontinuous glass fibers, continuous or discontinuous carbon fibers, and mixtures thereof.

The concentration of the reinforcement material used in the present invention may range generally from about 10 wt % to about 90 wt % in one embodiment, from about 15 wt % to about 85 wt % in another embodiment, and from
10 about 20 wt % to about 80 wt % in still another embodiment. The reinforcing material needs to have such a presence that the composite article meets electrical, thermal and mechanical performance targets for the industry. Too low or too high an amount of reinforcing material will cause detrimental issues in the aforementioned performances.

15 A beneficial optional additive that can be added to form the gel layer may include for example monofunctional reactive diluents (including for example cresyl glycidyl ether, butyl glycidyl ether, and the like), di-functional reactive diluents (including for example butanediol diglycidyl ether, butane dioxide, and the like), non-reactive diluents (including for example dibutyl phthalate and phenolic compounds, and
20 the like) which is capable of modifying the viscosity of the gel-layer to be advantageous for processing.

The concentration of the optional additive, when used in the present invention, may range generally from 0 wt % to about 5 wt % in one embodiment, from about 0.1 wt % to about 3 wt % in another embodiment, from about 0.5 wt % to about
25 1 wt % in still another embodiment. If too much viscosity modifier is used (e.g., > 5 wt %), the mechanical properties of the formulation may be adversely impacted.

A beneficial optional additive that can be added to form the gel layer may include for example a gel or a cure accelerator which is adapted to accelerating the rate of crosslinking within the curing formulation.

The concentration of the optional additives used in the present invention may range generally from 0 wt % to about 3 wt % in one embodiment, from about 0.1 wt % to about 2 wt % in another embodiment, and from about 0.5 wt % to about 1 wt % in still another embodiment. If too much gel or cure accelerator is added then the
5 formulation may be too reactive and a homogenous gel-layer may not be achieved.

In general, the process for manufacturing a fiber-reinforced composite article useful for contaminant removal such as radionuclide removal includes the steps of:

(A) disposing a gel material layer onto the surface of a mandrel; (B) introducing a fiber
10 reinforcement into a polymer resin impregnation means; (C) impregnating the fiber reinforcement of step (B) with a polymer resin to form a polymer fiber-reinforced layer material; (D) disposing the resin impregnated fiber-reinforced layer material of step (C) onto the surface of the gel material layer of (A); and (E) bonding polymer gel material
15 layer to the polymer fiber-reinforced layer material by curing the combination of the gel material layer and the resin impregnated fiber-reinforced layer material to form at least one single layer of a fiber-reinforced composite including at least three regions in said at least one single layer. The three regions include the following:

(a) at least one first polymer fiber-free region containing material adapted for removing contaminants, the contaminant removal material integrated into
20 the first polymer fiber-free region;

(b) at least one second polymer fiber-rich region containing fiber reinforcement material; and

(c) at least one third polymer boundary region containing a portion of the first polymer fiber-free region and a portion of the second polymer fiber-rich
25 region.

The first polymer fiber-free region includes an inner surface and an outer surface; and the second polymer fiber-rich region includes an inner surface and an outer surface. The outer surface of the first polymer fiber-free region is integrally bonded to the inner surface of the second polymer fiber-rich region forming the at least

one third polymer boundary region disposed between the first polymer fiber-free region and the second polymer fiber-rich region. The third polymer boundary region further comprises a contiguous boundary of a non-delineated width between the first polymer fiber-free region and the second polymer fiber-rich region. And, the first polymer
5 fiber-free region is integrally attached to the second polymer fiber-rich region such that the first polymer fiber-free region and second polymer fiber-rich region are infused together forming the at least one third polymer boundary region.

More specifically, the first step of the process includes admixing the required components to make the gel layer such as for example: (i) an epoxy resin, (ii)
10 a curing agent such as an amine curing agent for curing the epoxy resin, (iii) a particulate material; and
(iv) any optional compounds, for example, a dispersing aid. Then the mixture can be processed under conditions for forming a gel layer including heating the above mixture at a predetermined temperature and time to form an effective gel layer. The
15 temperature of heating can generally be in the range of from about 15 °C to about 60 °C in one embodiment, from about 20 °C to about 40 °C in another embodiment, and from about
22 °C to about 30 °C in still another embodiment. If the temperature of the formulation is too low, this may cause a significant increase in viscosity (e.g., > 40,000 mPa-s)
20 resulting in an inability to process the gel layer onto the mandrel. If the temperature of the formulation is too high, this may cause a significant increase in the reactivity of the gel layer and may not allow sufficient time to apply the gel layer to the mandrel before curing.

The heating time to form the gel layer may be, for example, generally
25 from about 5 min to about 120 min in one embodiment, from about 10 min to about 60 min in another embodiment, and from about 15 min to about 45 min in still another embodiment. In general, the heating time for the gel layer will depend on the composition and reactivity of the gel layer. Too high of a heating time may increase the temperature such that the curing reaction is induced and the gel layer cannot be
30 properly applied to the mandrel. Too low of a heating temperature and the viscosity of

the gel layer formulation may be too high such that the gel layer may not be homogenously applied to the mandrel.

The process of the present invention for forming the gel layer may be a batch process, an intermittent process, or a continuous process using equipment well known to those skilled in the art.

Once the composition for the gel layer is made, the gel layer formulation is applied to the mandrel of a filament winding process.

The process includes the step of admixing the compounds or components required to make the second polymer fiber-rich composite layer of the composite: (i) a polymer resin, (ii) a curing agent for curing the resin, and (iii) a fiber reinforcement material. Then the mixture can be processed under conditions for forming a fiber-reinforced layer generally including the steps of introducing a fiber reinforcement into a polymer resin impregnation means; and impregnating the fiber reinforcement with a polymer resin to form a second polymer fiber-reinforced layer material.

Generally, to form the polymer fiber-reinforced layer, the impregnation of the fiber reinforcement with a polymer resin is carried out at a predetermined temperature and time to form an effective fiber-reinforcement layer. The temperature of heating can generally be in the range of from about 15 °C to about 40 °C in one embodiment, from about 20 °C to about 35 °C in another embodiment, and from about 25 °C to about 30 °C in still another embodiment. Any heating outside of the above range may cause adverse effects to the desired rheological behavior of the mixed formulation. For example, temperatures below 15 °C may cause the mixed formulation's viscosity to increase to a level that is un-usable in the methods described above as well as slowing the epoxy-amine reaction to such a low rate that the gel-point of the material cannot be reached. And, temperatures above 40 °C may lower the viscosity to such a state that the material will drip from the mandrel and may not form a homogenous layer on the desired surface of the composite article. Additionally, a temperature higher than 40 °C may prematurely induce the autocatalytic curing reaction and render the mixed formulation un-usable.

If the composite article is heated for too little time, the cross-linking reaction associated with thermoset matrices may not be complete with the resulting effect of producing an underperforming article.

5 The process of the present invention for forming the fiber reinforced layer may be a batch process, an intermittent process, or a continuous process using equipment well known to those skilled in the art. The heating time to form the fiber reinforced composite may be, for example, generally from about 1 hour to about 24 hours in one embodiment, from about 1.5 hour to about 12 hours in another embodiment, and from about 2 hours to about 8 hours in still another embodiment.

10 Upon bonding the combined fiber-reinforced layer and gel layer to form a single composite article a first polymer fiber-free region, a second polymer fiber-rich region, and a third polymer boundary region is formed in the single composite article.

As aforementioned, the first polymer fiber-free region includes an inner surface and an outer surface; and the second polymer fiber-rich region includes an inner surface and an outer surface. The outer surface of the first polymer fiber-free region is integrally bonded to the inner surface of the second polymer fiber-rich region forming the at least one third polymer boundary region disposed between the first polymer fiber-free region and the second polymer fiber-rich region. The third polymer boundary region further comprises a contiguous boundary of a non-delineated width between the first polymer fiber-free region and the second polymer fiber-rich region. And the first polymer fiber-free region is integrally attached to the second polymer fiber-rich region such that the first polymer fiber-free region and second polymer fiber-rich region are infused together forming the at least one third polymer boundary region.

25 Some non-limiting examples of enduse applications for the composite product of present invention may include, for example, in manufacturing an article by filament winding, pultrusion, infusion, hand lay-up, or a combination of such methods. The composite article can be for example a conduit, a pipe or piping for use in downhole wells in the oil and gas industry; or a pipe for flowing a liquid fluid therein and removing contaminants (e.g., a radionuclide) present in the liquid fluid from the liquid such as contaminated fluid from hydraulic fracturing operations.

Exemplary embodiments that may incorporate any or all of the above-discussed features, include, the following:

A fiber-reinforced composite article useful for contaminant removal comprising at least one single layer of a fiber-reinforced composite including the following regions in said at least one single layer: (a) at least one first polymer fiber-free region containing material adapted for removing contaminants, said contaminant removal material integrated into the first polymer fiber-free region; said first polymer fiber-free region including an inner surface and an outer surface; (b) at least one second polymer fiber-rich region containing fiber reinforcement material; said second polymer fiber-rich region including an inner surface and an outer surface; and (c) at least one third polymer boundary region containing a portion of the first polymer fiber-free region and a portion of the second polymer fiber-rich region. Whereas, the outer surface of the first polymer fiber-free region is integrally bonded to the inner surface of the second polymer fiber-rich region forming the at least one third polymer boundary region disposed between the first polymer fiber-free region and the second polymer fiber-rich region; wherein the third polymer boundary region further comprises a contiguous boundary of a non-delineated width between the first polymer fiber-free region and the second polymer fiber-rich region; and wherein the first polymer fiber-free region is integrally attached to the second polymer fiber-rich region such that the first polymer fiber-free region and second polymer fiber-rich region are infused together forming the at least one third polymer boundary region.

A process for manufacturing a fiber-reinforced composite article useful for contaminant removal at least one single layer of a fiber-reinforced composite comprising the steps of: (i) providing a formulation for forming at least one first polymer fiber-free gel layer; (ii) applying the first polymer fiber-free gel layer formulation of (i) onto a mandrel of a filament winding process such that the polymer fiber-free gel layer formulation forms a polymer fiber-free gel layer of a predetermined thickness on the mandrel; (iii) providing a formulation for forming at least one second polymer fiber-rich layer; (iv) applying the second polymer fiber-rich layer formulation of (iii) onto the surface of the polymer fiber-free gel layer produced in step (ii) such that the second polymer fiber-rich layer formulation forms a second polymer fiber-rich

layer of a predetermined thickness disposed on the first polymer fiber-free gel layer which is disposed on the mandrel; and (v) curing the first polymer fiber-free gel layer and second polymer fiber-rich layer to form at least one single layer of a fiber-reinforced composite; wherein the at least one single layer of a fiber-reinforced

- 5 composite includes the following regions in said single layer: (a) at least one first polymer fiber-free region containing material adapted for removing contaminants, said contaminant removal material integrated into the first polymer fiber-free region; said first polymer fiber-free region including an inner surface and an outer surface; (b) at least one second polymer fiber-rich region containing fiber reinforcement material; said
10 second polymer fiber-rich region including an inner surface and an outer surface; and (c) at least one third polymer boundary region containing a portion of the first polymer fiber-free region and a portion of the second polymer fiber-rich region.

- Whereas, the outer surface of the first polymer fiber-free region is integrally bonded to the inner surface of the second polymer fiber-rich region forming the at least one third
15 polymer boundary region disposed between the first polymer fiber-free region and the second polymer fiber-rich region; wherein the third polymer boundary region further comprises a contiguous boundary of a non-delineated width between the first polymer fiber-free region and the second polymer fiber-rich region; and wherein the first polymer fiber-free region is integrally attached to the second polymer fiber-rich region
20 such that the first polymer fiber-free region and second polymer fiber-rich region are infused together forming the at least one third polymer boundary region.

- An apparatus for manufacturing a fiber-reinforced composite article useful for contaminant removal comprising: (I) a means for disposing a gel material layer onto the surface of a mandrel; (II) a means for introducing a fiber reinforcement
25 into a resin impregnation means; (III) a resin impregnation means for impregnating the fiber reinforcement of (II) with a polymer resin to form a polymer fiber-reinforced layer material; (IV) a means for disposing the resin impregnated fiber-reinforced layer material of (III) onto the surface of the gel material layer of (I); and (V) a means for curing the combination of the gel material layer and the resin impregnated fiber-
30 reinforced layer material to form at least one single layer of a fiber-reinforced composite including the following regions in said at least one single layer: (a) at least one first polymer fiber-free region containing material adapted for removing

contaminants, said contaminant removal material integrated into the first polymer fiber-free region; said first polymer fiber-free region including an inner surface and an outer surface; (b) at least one second polymer fiber-rich region containing fiber reinforcement material; said second polymer fiber-rich region including an inner surface and an outer surface; and (c) at least one third polymer boundary region containing a portion of the first polymer fiber-free region and a portion of the second polymer fiber-rich region. Whereas, the outer surface of the first polymer fiber-free region is integrally bonded to the inner surface of the second polymer fiber-rich region forming the at least one third polymer boundary region disposed between the first polymer fiber-free region and the second polymer fiber-rich region; wherein the third polymer boundary region further comprises a contiguous boundary of a non-delineated width between the first polymer fiber-free region and the second polymer fiber-rich region; and wherein the first polymer fiber-free region is integrally attached to the second polymer fiber-rich region such that the first polymer fiber-free region and second polymer fiber-rich region are infused together forming the at least one third polymer boundary region.

A process for manufacturing a fiber-reinforced composite article useful for contaminant removal comprising the steps of: (A) disposing a gel material layer onto the surface of a mandrel; (B) introducing a fiber reinforcement into a polymer resin impregnation means; (C) impregnating the fiber reinforcement of step (B) with a polymer resin to form a polymer fiber-reinforced layer material; (D) disposing the resin impregnated fiber-reinforced layer material of step (C) onto the surface of the gel material layer of (I); and (E) bonding polymer gel material layer to the polymer fiber-reinforced layer material by curing the combination of the gel material layer and the resin impregnated fiber-reinforced layer material to form at least one single layer of a fiber-reinforced composite including the following regions in said at least one single layer: (a) at least one first polymer fiber-free region containing material adapted for removing contaminants, said contaminant removal material integrated into the first polymer fiber-free region; said first polymer fiber-free region including an inner surface and an outer surface; (b) at least one second polymer fiber-rich region containing fiber reinforcement material; said second polymer fiber-rich region including an inner surface and an outer surface; and (c) at least one third polymer

boundary region containing a portion of the first polymer fiber-free region and a portion of the second polymer fiber-rich region. Whereas, the outer surface of the first polymer fiber-free region is integrally bonded to the inner surface of the second polymer fiber-rich region forming the at least one third polymer boundary region

5 disposed between the first polymer fiber-free region and the second polymer fiber-rich region; wherein the third polymer boundary region further comprises a contiguous boundary of a non-delineated width between the first polymer fiber-free region and the second polymer fiber-rich region; and wherein the first polymer fiber-free region is integrally attached to the second polymer fiber-rich region such that the first polymer

10 fiber-free region and second polymer fiber-rich region are infused together forming the at least one third polymer boundary region. The process may further provide for the exposed surface area of the material adapted for removing contaminants is increased by the further steps of: (v) applying a pre-processing treatment to the surface upon which the composite article is formed; and (vi) applying a post-processing treatment to the

15 composite article. The post-processing treatment may be a mechanical, thermal, electrical or chemical post-processing method.

A process for removing contaminants from a liquid fluid in contact with a fiber-reinforced composite article comprising the steps of: (α) providing a fiber-reinforced composite article useful for contaminant removal comprising at least one

20 single layer of a fiber-reinforced composite including the following regions in said at least one single layer: (a) at least one first polymer fiber-free region containing material adapted for removing contaminants, said contaminant removal material integrated into the first polymer fiber-free region; said first polymer fiber-free region including an inner surface and an outer surface; (b) at least one second polymer fiber-rich region

25 containing fiber reinforcement material; said second polymer fiber-rich region including an inner surface and an outer surface; and (c) at least one third polymer boundary region containing a portion of the first polymer fiber-free region and a portion of the second polymer fiber-rich region. Whereas, the outer surface of the first polymer fiber-free region is integrally bonded to the inner surface of the second

30 polymer fiber-rich region forming the at least one third polymer boundary region disposed between the first polymer fiber-free region and the second polymer fiber-rich region; wherein the third polymer boundary region further comprises a contiguous

boundary of a non-delineated width between the first polymer fiber-free region and the second polymer fiber-rich region; and wherein the first polymer fiber-free region is integrally attached to the second polymer fiber-rich region such that the first polymer fiber-free region and second polymer fiber-rich region are infused together forming the
5 at least one third polymer boundary region. Further comprising, (β) contacting a liquid fluid with the first polymer fiber-free region containing material adapted for removing contaminants such the material adapted for removing contaminants in the first polymer fiber-free region adsorbs one or more contaminants from the liquid fluid.

EXAMPLES

10 The following examples and comparative examples further illustrate the present invention in more detail but are not to be construed to limit the scope thereof.

In the following Examples, various materials, terms and designations are used and are explained as follows:

EEW stands for epoxide equivalent weight.

15 AHEW stands for amine hydrogen equivalent weight.

D.E.R. 383 is an epoxy resin having an EEW of 171 and commercially available from The Dow Chemical Company.

D.E.N. 438 is an epoxy resin having an EEW of 179 and commercially available from The Dow Chemical Company.

20 VORAFORCE™ TW 120 is a formulated amine hardener having an AHEW of 36 and commercially available from The Dow Chemical Company.

BYK 940 is a dispersion-aiding additive and commercially available from Altana.

BaSO₄ powder was obtained from Excalibar Minerals.

25 Standard measurements, analytical equipment and methods were used in the Examples as follows:

EEW Measurements

The EEW of the resin was measured according to the procedure described in ASTM D-1652 (2011).

AHEW Measurements

5 The AHEW of the resin was calculated after finding the amine value according to the procedure described in ISO 9702 (1996).

Viscosity Measurements

The viscosity of the resin was measured according to the procedure described in ASTM D-445(2015) at 25°C.

General Procedure of Filament Winding Process

10 A composite pipe of the present invention can be manufactured using a filament winding process. Filament winding is one of the more important composite production methods in terms of number of users and total number of fabricated parts. The filament winding process begins with fiber tows coming from spools of glass or carbon fibers mounted on a creel. The fibers are gathered together and collected
15 through a type of fiber guide (i.e., a “comb”) to form a band. The number of the fibers brought together determines the band width. The band is pulled through a resin bath (containing a resin and a hardener mixed together such that the formulation is active). The resin from the resin bath impregnates the pulled fiber tow. The fibers are then drawn through a roller or wiper system to achieve the desired resin content on the
20 fibers; and then the fibers are drawn through a payoff. The “payoff” is the point at which the fiber contacts a moving carriage and directs the fibers on to a rotating mandrel. This method of production is efficient for producing any type of cylindrical part. Furthermore, as the complexity and capability of filament winding machines increases other non-cylindrical parts can also be wound using a filament winding
25 method.

General Procedure of Hand-Lay Up

A composite article of the present invention, alternatively, can be manufactured through a hand lay-up method utilizing two different production steps. Hand lay-up is the simplest and oldest open molding method of the composite fabrication processes. It is a low volume, labor intensive method suited especially for large components. Glass, carbon or other reinforcing mat or woven fabric or roving is positioned manually in the open mold, and resin is poured, brushed, or sprayed over and into the glass plies. Entrapped air is removed manually with squeegees or rollers to complete the laminates structure. Curing is initiated by a catalyst in the resin formulation, which hardens the fiber reinforced resin composite without external heat. Post cure to achieve higher mechanical properties is often required.

Example 1 – Manufacture of Composite Article Via Filament Winding

Two different formulated compositions were used to produce a single composite article using a filament winding process. The two compositions are described in Table I. The two formulations or compositions were designed for advantageously having a fiber-free (i.e., resin-rich) layer containing barium sulfate particles near the surface of the composite article (“first composition”) and a fiber-rich (“second composition”) layer chemically bonded to the resin-rich layer providing mechanical reinforcement.

The first composition (“Gel Layer” in Table I), was applied as a gel layer to a rotating mandrel and was designed to have high initial viscosity (e.g., > 20,000 mPa-s) to prevent sagging and dripping during application of gel layer onto the mandrel; and a fast gel time (e.g., < 1 hour at 25°C) to advantageously allow the gel layer to be processed more readily.

The second composition (“Fiber-Reinforced Layer” in Table I) was designed as a low viscosity formulation (e.g., ~ 500 mPa-s) for a traditional open-bath filament winding manufacturing process. The low viscosity of the second composition ensures thorough and homogenous fiber wet out during the composite article manufacture. The second composition has a longer gel time (e.g., > 6 hours at 25°C)

than the first composition; and has desirable toughness properties upon curing (e.g., K_{IC} Mode Fracture Toughness $\sim 0.75 \text{ MPa}\cdot\text{m}^{1/2}$).

5 Table I – Formulations for Gel layer and Fiber-Reinforced Layer for Use in a Filament Winding System

Component	Gel Layer (wt %)	Fiber-Reinforced Layer (wt %)
D.E.R. 383	0.0	71.6
D.E.N. 438	20.8	0.0
1,4 butanediol diglycidyl ether	0.0	11.7
VORAFORCE™ TW 120	4.2	16.7
BaSO ₄ powder	75.0	0.0
Total	100	100

Example 2 – Manufacture of Composite Article Via Hand Lay-Up

10 In this Example 2, two different polymer compositions are used to produce a composite article using a hand lay-up process. The two polymer compositions are described in Table II. The two formulations or compositions are designed for advantageously having a fiber-free (i.e., resin-rich) layer containing barium sulfate particles near the surface of the composite article (“first composition”) and a fiber-rich (“second composition”) layer chemically bonded to the resin-rich layer
15 providing mechanical reinforcement.

The first polymer composition (“Gel Layer” in Table II), is applied as a gel layer to a substrate and is designed to have high initial viscosity (e.g., $> 20,000 \text{ mPa}\cdot\text{s}$) to prevent sagging and dripping during application of gel layer; and a fast gel time (e.g.,
20 $< 1 \text{ hour at } 25^\circ\text{C}$) to advantageously allow the gel layer to be processed more readily.

The second polymer composition (“Fiber-Reinforced Layer” in Table II) is a commercially available conventional formulation have a low viscosity for homogenous fiber bundle impregnation; and exhibiting a long gel time (e.g., $> 6 \text{ hours at } 25^\circ\text{C}$).

25 Table II – Formulations for Gel layer and Fiber-Reinforced Layer for Use in a Hand Lay-Up System

Component	Gel-Layer (wt %)	Fiber-Reinforced Layer (wt %)
D.E.R. 383	0.0	69.5
D.E.N. 438	29.8	0.0
1,4 butanediol diglycidyl ether	0.0	5.2
methyl-p-toluene sulfonate	0.1	0.2
polyetherdiamine, 230 MW	10.1	25.1
BaSO ₄ powder	60.0	0.0
Total	100	100

Examples 3-5 – Absorption of Radium-226

Three trials were run to quantify the amount of radionuclide removal using a fiber-reinforced composite of the present invention as follows:

5 General Procedure of Testing

In general, the experiments related to the absorption of Radium-226 (Ra-226) were carried out using two granular materials containing different mass fractions of barium sulfate (GM1 and GM2). The three trials were: (1) both materials were tested at 50 degrees Celsius (°C), 70 °C and 90 °C, (2) material GM1 in brine and in a
10 modified brine lacking barium sulfate are tested at 90 °C, and (3) barium sulfate in brine and in a modified brine lacking barium sulfate are tested at 90 °C.

The general procedure included contacting the two materials with brine containing Ra-226 at three temperatures. The brine contained chlorides of calcium, sodium and barium. Samples of brine were taken at various times and analyzed to
15 assess the amount of Ra-226 remaining in the brine. The amount of Ra-226 absorbed by the materials was assessed at the end of the experiment.

Samples of material and brine were placed in 500 ml glass bottles and held at a fixed temperature. A water bath was used for the 50 °C trial and electric ovens were used for the 70 °C and the 90 °C trials. The mixture was mixed by swirling
20 several times during each experiment.

A standard solution of Ra-226, commercially available from Isotope Products Laboratories, was diluted with dilute nitric acid to obtain a working solution. Portions of the working solution were then dispensed for each of the trials by pipetting.

One-liter lots of brine are prepared by weighing. The brine contains 5.0 wt %, 2.6 wt %, and 0.07 wt % of NaCl, CaCl₂ and BaCl₂·2H₂O, respectively. The pH of the brine was adjusted to between 7.5 and 8.0 using solutions of sodium hydroxide and hydrochloric acid.

5 A portion of brine was weighed out for each test. A solution (2.457 milliliters (mL)) containing approximately 5,000 picoCuries of Ra-226 was added to the brine, and the pH of the brine was readjusted. One of the brine portions was added to a pre-weighed sample of material to start each test.

10 The detection of Ra-226 in brine samples was determined by Liquid Scintillation Counting (LSC). After the Ra-226 exposure to the fiber composite was complete, the detection of Ra-226 captured in the contaminant-capturing particles of the material was determined by Gamma-ray Spectrometry.

Before LSC, each aliquot was gently evaporated in order to expel Rn-222, which interfered with the Ra-226 measurement. Two counting windows were used: one registered counts due to both Ra-226 and Rn-222 and the other registered counts only due to Rn-222. A correction factor was established using water from a Radon generator and was used to correct for Rn-222 interference on Ra-226.

Example 3 – Trial 1

20 45 g of material and 180 g of brine are used for each test. At each sampling, the bottles are weighed and aliquots are withdrawn from opened bottles using an air displacement pipette. After the final sampling, the material is removed from the exposure bottle by slurrying with deionized water and was then briefly rinsed with further deionized water before packaging for gamma-ray spectrometry. Results were corrected for the effects of pipetting hot liquids and for losses due to evaporation. Four control preparations were tested to assess any contribution from the materials used. 25 The results of the first trial are described in Tables III and IV.

Table III – Results by Liquid Scintillation Counting

<u>Medium</u>	<u>Temperature (°C)</u>	<u>Time</u>	<u>Fraction Remaining^(a)</u>	<u>Uncertainty^(b)</u>
GM1	50	1 hour	0.99	0.03

		4 hours	0.98	0.03
		3 days	0.89	0.03
		7 days	0.89	0.03
GM2	50	1 hour	1.00	0.03
		4 hours	0.89	0.03
		3 days	0.86	0.03
		7 days	0.89	0.03
GM1	70	1 hour	0.99	0.03
		4 hours	0.96	0.03
		3 days	0.95	0.03
		7 days	1.02	0.03
GM2	70	1 hour	0.96	0.03
		4 hours	0.93	0.03
		3 days	0.91	0.03
		7 days	0.86	0.03
GM1	90	1 hour	1.04	0.03
		4 hours	1.06	0.03
		3 days	0.88	0.03
		7 days	0.80	0.02
GM2	90	1 hour	1.02	0.03
		4 hours	1.05	0.03
		3 days	0.99	0.03
		7 days	1.03	0.03

Notes for Table III:

(a) count rate divided by the count rate for a sample taken at the start of the experiment

(b) 1 standard deviation, computed from counting statistics

- 5 The results were corrected for interference due to Radon, losses due to evaporation and the effect of hot solutions on the operation of pipettes. Uncertainty arising from pipetting could not be assessed and was not included in the estimates given above.

Table IV – Gamma-ray Spectrometry.

<u>Medium</u>	<u>Temperature (°C)</u>	<u>Ra-226 Activity (Bq)</u>	<u>1 Standard Deviation</u>	<u>% of Original Ra- 226 Activity</u>	<u>1 Standard Deviation</u>
GM1	70	10.3	0.5	5.6	0.3
GM2	70	19.8	0.6	10.7	0.3
GM1	90	12.8	0.4	6.9	0.2

Example 4 – Trial 2

90 g of material GM1 and 360 g of brine were used for each test. One lot of brine contained barium, the other did not. In both cases, the pH was adjusted to 7.5 to 8.0. The contact was carried out at 90 °C. Each portion of material was rinsed
 5 three times with deionized water to remove fines before addition of brine. Slight cloudiness was observed in the final rinse.

At each sampling, the bottles were weighed and aliquots were withdrawn from bottles using a syringe and a thin tube that passed through a small hole in the bottle cap; and placed in pre-weighed vials. The amount collected was
 10 determined by re-weighing the vials, and was included in calculations.

The brine was sampled before mixing with material, immediately after mixing, at 3 days and at 7 days. Duplicate aliquots were taken at 3 days and 7 days. After the final sampling, the brine was thoroughly drained from the material and the material was then packaged for gamma-ray spectrometry. The results of the second
 15 trial are described in Tables V and VI.

Table V – Liquid Scintillation Counting

<u>Material</u>	<u>Brine</u>	<u>Temperature (°C)</u>	<u>Time</u>	<u>Fraction Remaining^(a)</u>	<u>Uncertainty^(b)</u>
GM1	With Ba	90	before mixing	1.00	
			after mixing	0.93	0.02
			7 days	0.78, 0.79	0.02
GM1	Without Ba	90	before mixing	1.00	
			after mixing	0.86	0.01
			3 days	0.49, 0.50	0.01
			7 days	0.51, 0.51	0.01

Notes for Table V:

^(a) count rate divided by the count rate for a sample taken before the start of the experiment

20 ^(b) 1 standard deviation, computed from counting statistics

Table VI – Gamma-ray Spectrometry

<u>Medium</u>	<u>Brine</u>	<u>Ra-226 Activity (Bq)</u>	<u>1 Standard Deviation</u>	<u>% of Original Ra-226 Activity</u>	<u>1 Standard Deviation</u>
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<u>Medium</u>	<u>Brine</u>	<u>Ra-226 Activity (Bq)</u>	<u>1 Standard Deviation</u>	<u>% of Original Ra-226 Activity</u>	<u>1 Standard Deviation</u>
GM1	With Ba	42.5	1.3	26.1	0.9
GM1	Without Ba	98.9	1.7	56.6	1.3

Example 5 – Trial 3

0.72 g of barium sulfate and 360 g of brine were used for each test. One lot of brine contained barium, the other did not. In both cases, the pH was adjusted to 7.5 to 8.0. The contact was carried out at 90 °C.

At each sampling, the bottles were weighed and aliquots were withdrawn from bottles using a syringe and a thin tube that passed through a small hole in the bottle cap, and placed in pre-weighed vials. The amount collected was determined by re-weighing the vials, and was included in calculations.

The brine was sampled before mixing with barium sulphate, immediately after mixing at 3 days. Duplicate aliquots were taken at 3 days. As the barium sulphate was initially too finely divided to settle, the initial portion was filtered. By 3 days, filtering was unnecessary.

After the final sampling, the barium sulfate was collected by filtering, using filtrate to collect as much of the still very finely divided solid as possible. There may have been small losses to the walls of the bottle. The filters were then packaged for gamma-ray spectrometry. The results of the third trial are described in Tables VII and VIII.

Table VII – Liquid Scintillation Counting

<u>Material</u>	<u>Brine</u>	<u>Temperature (°C)</u>	<u>Time</u>	<u>Fraction Remaining^(a)</u>	<u>Uncertainty^(b)</u>
BaSO ₄	With Ba	90	before mixing	1.00	
			after mixing	0.96	0.02
			3 days	0.73, 0.69	0.02
BaSO ₄	Without Ba	90	before mixing	1.00	
			after mixing	0.46	0.02
			3 days	0.047, 0.047	0.009

Notes for Table VII:

^(a) count rate divided by the count rate for a sample taken before the start of the experiment

^(b) 1 standard deviation, computed from counting statistics

Table VIII – Gamma-ray Spectrometry

<u>Medium</u>	<u>Brine</u>	<u>Ra-226 Activity (Bq)</u>	<u>1 Standard Deviation</u>	<u>% of Original Ra-226 Activity</u>	<u>1 Standard Deviation</u>
BaSO ₄	With Ba	44.8	0.6	31.5	0.7
BaSO ₄	Without Ba	122	2	85	2

WHAT IS CLAIMED IS:

1. A fiber-reinforced composite article useful for contaminant removal comprising at least one single layer of a fiber-reinforced composite including the following regions in said at least one single layer:

5 (a) at least one first polymer fiber-free region containing material adapted for removing contaminants, said contaminant removal material integrated into the first polymer fiber-free region; said first polymer fiber-free region including an inner surface and an outer surface;

(b) at least one second polymer fiber-rich region containing fiber reinforcement material; said second polymer fiber-rich region including an inner
10 surface and an outer surface; and

(c) at least one third polymer boundary region containing a portion of the first polymer fiber-free region and a portion of the second polymer fiber-rich region;

wherein the outer surface of the first polymer fiber-free region is
15 integrally bonded to the inner surface of the second polymer fiber-rich region forming the at least one third polymer boundary region disposed between the first polymer fiber-free region and the second polymer fiber-rich region; wherein the third polymer boundary region further comprises a contiguous boundary of a non-delineated width between the first polymer fiber-free region and the second polymer fiber-rich region;
20 and wherein the first polymer fiber-free region is integrally attached to the second polymer fiber-rich region such that the first polymer fiber-free region and second polymer fiber-rich region are infused together forming the at least one third polymer boundary region.

2. The composite of claim 1, wherein there fiber reinforced region
25 contains fiber reinforcement is glass, carbon, aramid, and mixtures thereof.

3. The composite of claim 1, wherein the fiber in the fiber-reinforced region is continuous reinforcing fibers or discontinuous reinforcing fibers.

4. The composite of claim 1, wherein the fiber orientation in the fiber-reinforced region is any orientation in a three-dimensional coordinate frame.

5 5. The composite of claim 1, wherein the polymer of the fiber-free region is a thermosetting resin, a thermoplastic resin, or a combination thereof.

6. The composite of claim 1, wherein the polymer of the fiber-reinforced region is a thermosetting resin, a thermoplastic resin, or a combination thereof.

10 7. The composite of claim 1, wherein the fiber-reinforced composite includes multi-functional materials, in addition to the contaminant removal materials, for increasing the mechanical, chemical, thermal and electrical properties of the fiber-reinforced composite.

15 8. The composite of claim 1, wherein the composite includes a plurality of fiber-free regions.

9. The composite of claim 1, wherein the composite includes a plurality of fiber-reinforced regions.

20 10. The composite of claim 1, wherein the composite includes a plurality of fiber-free regions and fiber-reinforced regions in any layered order in the composite.

11. The composite of claim 1, wherein the material adapted for removing contaminants is BaSO₄, MnO₂ or any combination thereof.

12. The composite of claim 1 comprising a conduit, pipe, or piping.

25 13. A process for manufacturing a fiber-reinforced composite article useful for contaminant removal at least one single layer of a fiber-reinforced composite comprising the steps of:

- (i) providing a formulation for forming at least one first polymer fiber-free gel layer;
- (ii) applying the first polymer fiber-free gel layer formulation of (i) onto a mandrel of a filament winding process such that the polymer fiber-free gel layer formulation forms a polymer fiber-free gel layer of a predetermined thickness on the
- 5 mandrel;
- (iii) providing a formulation for forming at least one second polymer fiber-rich layer;
- (iv) applying the second polymer fiber-rich layer formulation of (iii)
- 10 onto the surface of the polymer fiber-free gel layer produced in step (ii) such that the second polymer fiber-rich layer formulation forms a second polymer fiber-rich layer of a predetermined thickness disposed on the first polymer fiber-free gel layer which is disposed on the mandrel; and
- (v) curing the first polymer fiber-free gel layer and second polymer
- 15 fiber-rich layer to form at least one single layer of a fiber-reinforced composite; wherein the at least one single layer of a fiber-reinforced composite includes the following regions in said single layer:
- (a) at least one first polymer fiber-free region containing material adapted for removing contaminants, said contaminant removal material
- 20 integrated into the first polymer fiber-free region; said first polymer fiber-free region including an inner surface and an outer surface;
- (b) at least one second polymer fiber-rich region containing fiber reinforcement material; said second polymer fiber-rich region including an inner surface and an outer surface; and
- 25 (c) at least one third polymer boundary region containing a portion of the first polymer fiber-free region and a portion of the second polymer fiber-rich region;

wherein the outer surface of the first polymer fiber-free region is integrally bonded to the inner surface of the second polymer fiber-rich region forming the at least one third polymer boundary region disposed between the first polymer fiber-free region and the second polymer fiber-rich region; wherein the third polymer boundary region further comprises a contiguous boundary of a non-delineated width between the first polymer fiber-free region and the second polymer fiber-rich region; and wherein the first polymer fiber-free region is integrally attached to the second polymer fiber-rich region such that the first polymer fiber-free region and second polymer fiber-rich region are infused together forming the at least one third polymer boundary region.

14. The process of claim 13, wherein the fiber-free region is applied to the fiber-reinforced region by a manual lay-up method or an automated lay-up method.

15. The process of claim 13, wherein the fiber-reinforced composite is produced by a composite fabrication method including injection molding, compression molding, pultrusion, and filament winding.

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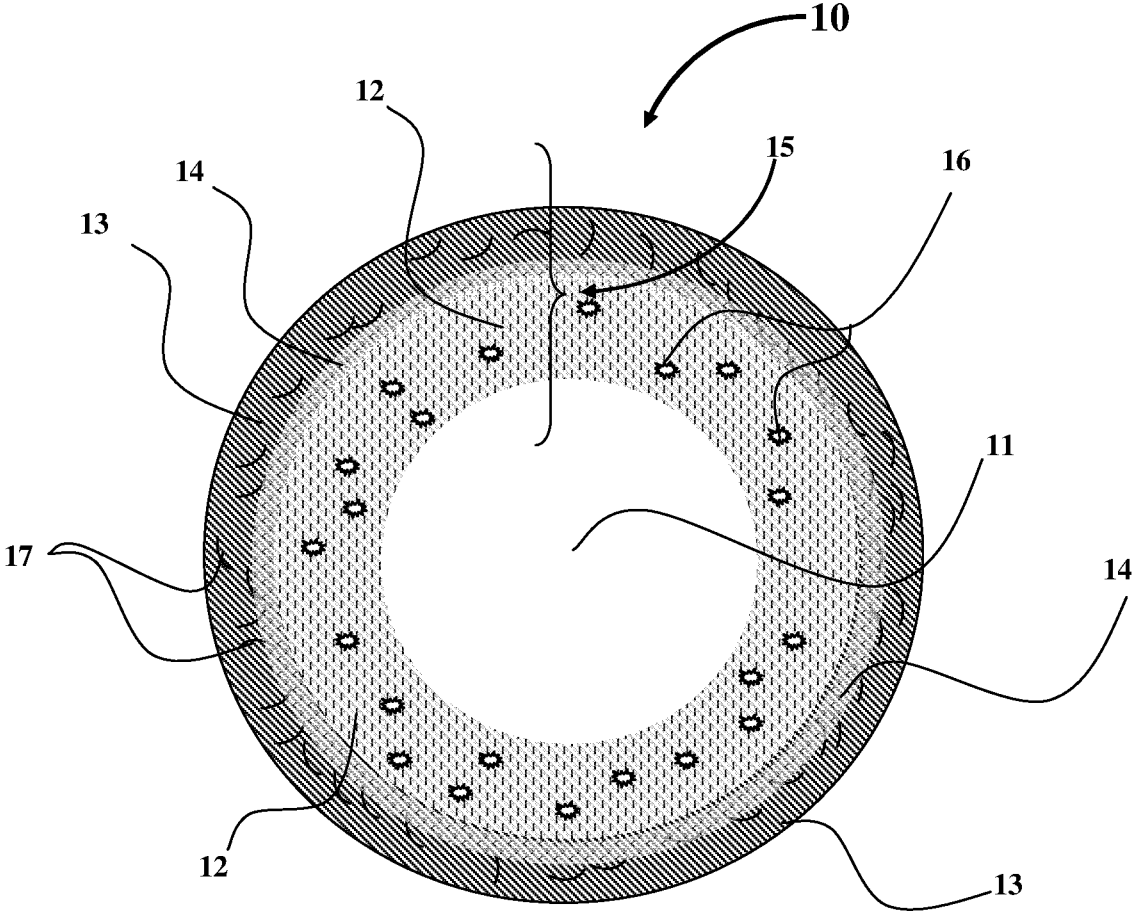


Fig. 1

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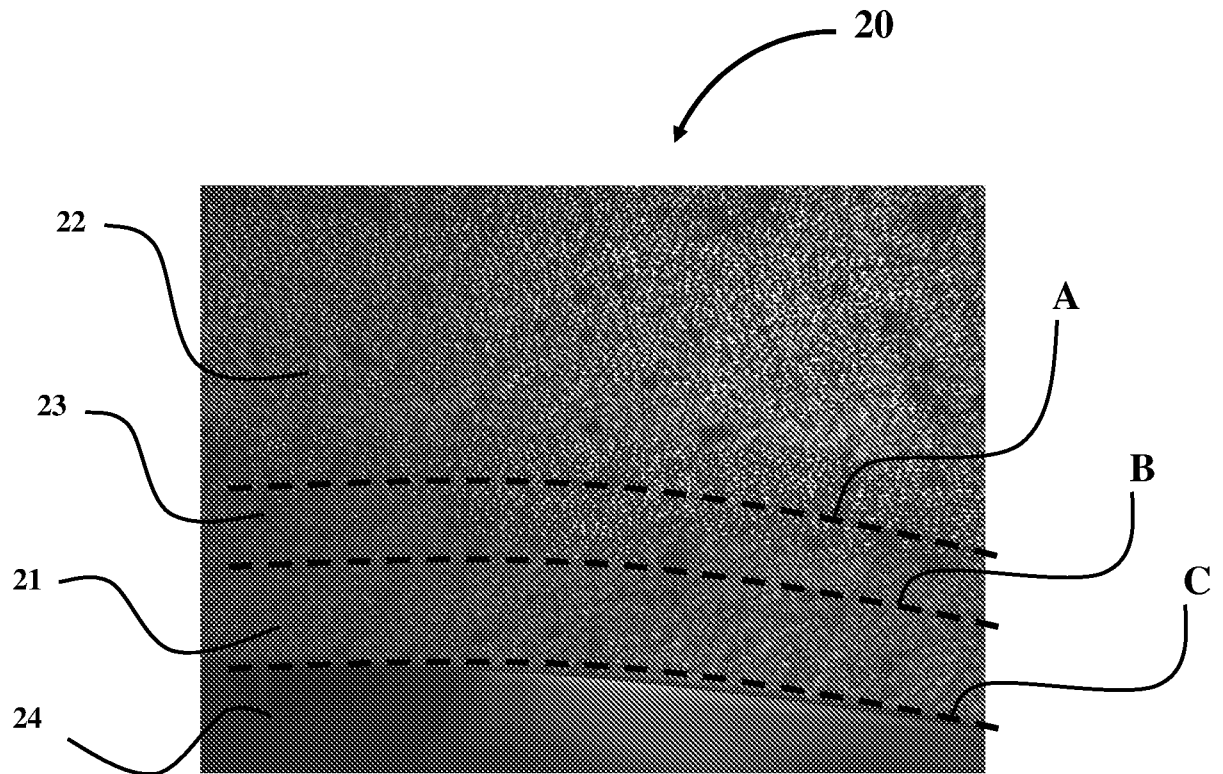


Fig. 2

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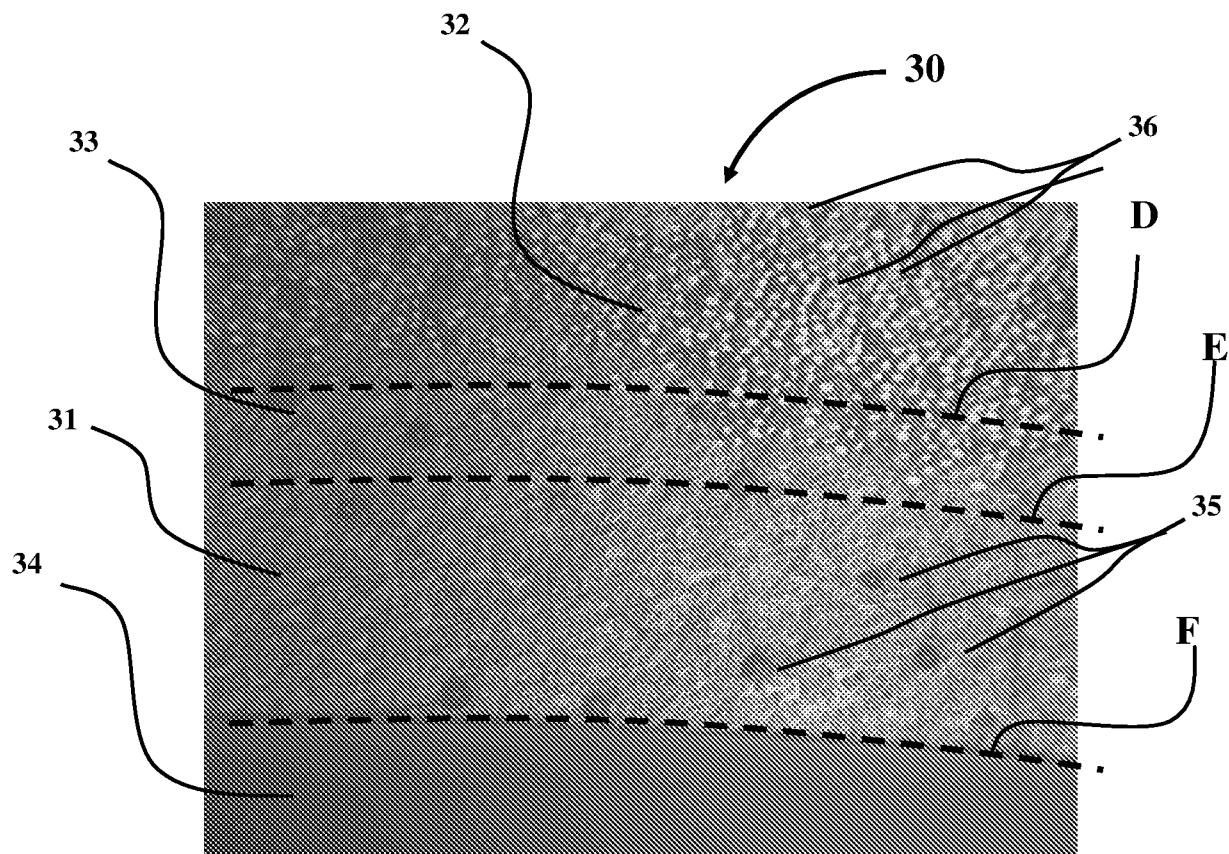


Fig. 3

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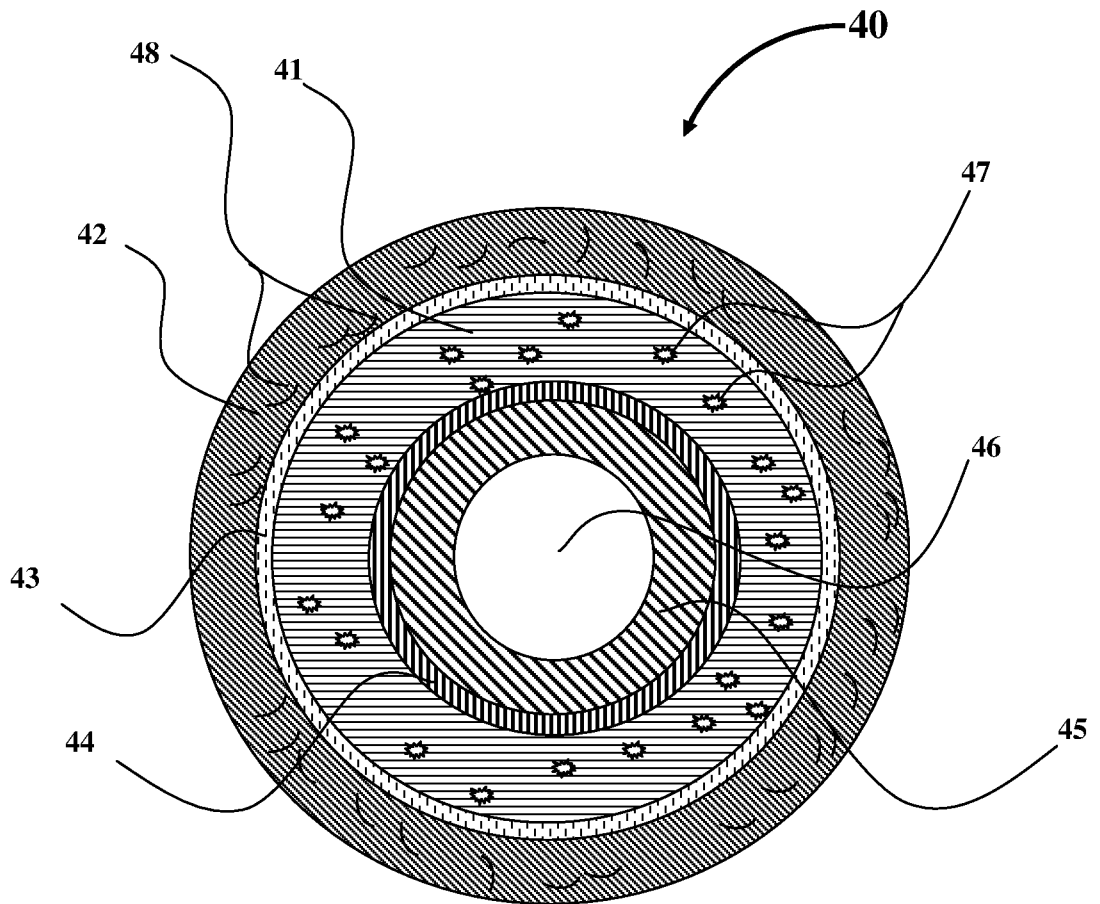


Fig. 4

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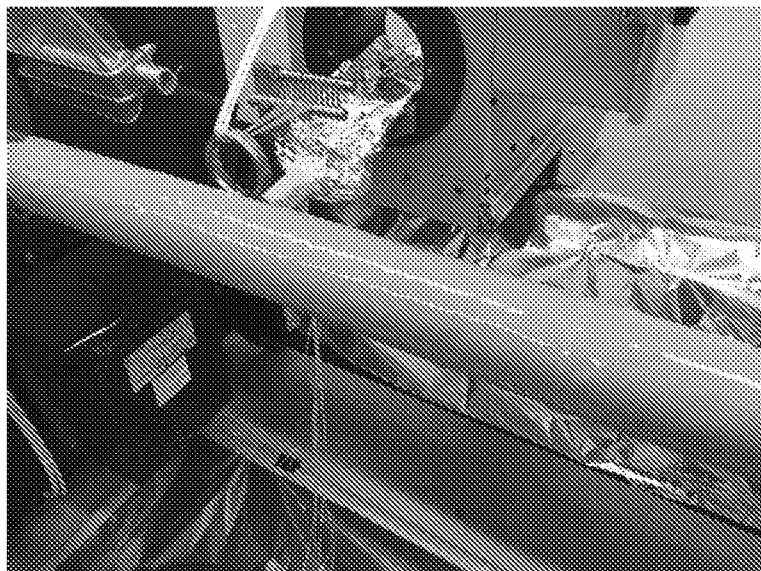


Fig. 5

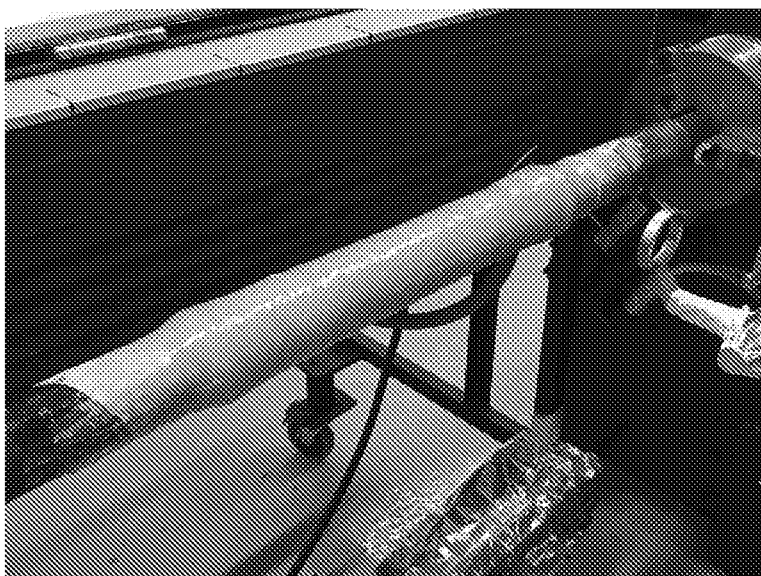


Fig. 6

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2016/038466

A. CLASSIFICATION OF SUBJECT MATTER

INV. C09K8/52 E21B21/06
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)

C09K E21B

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.
X	US 2009/200013 A1 (CRASTER BERNADETTE [CA] ET AL) 13 August 2009 (2009-08-13) paragraph 0021- paragraph 0032; fig. 2, figs. 4, 5, 6 & 8; paragraphs 0044 & 0045 -----	1-12
A	US 2013/180714 A1 (NEVIN DONALD [US]) 18 July 2013 (2013-07-18) paragraphs 0087-0094, figures 4-6 -----	1-12
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A	US 5 196 124 A (CONNOR JOHN A [US] ET AL) 23 March 1993 (1993-03-23) column 5 - column 6; claims 8, 14, 15 ----- -/-	11



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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"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

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Date of the actual completion of the international search

12 September 2016

Date of mailing of the international search report

20/09/2016

Name and mailing address of the ISA/

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Munro, Brian

INTERNATIONAL SEARCH REPORT

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