

US 20130133897A1

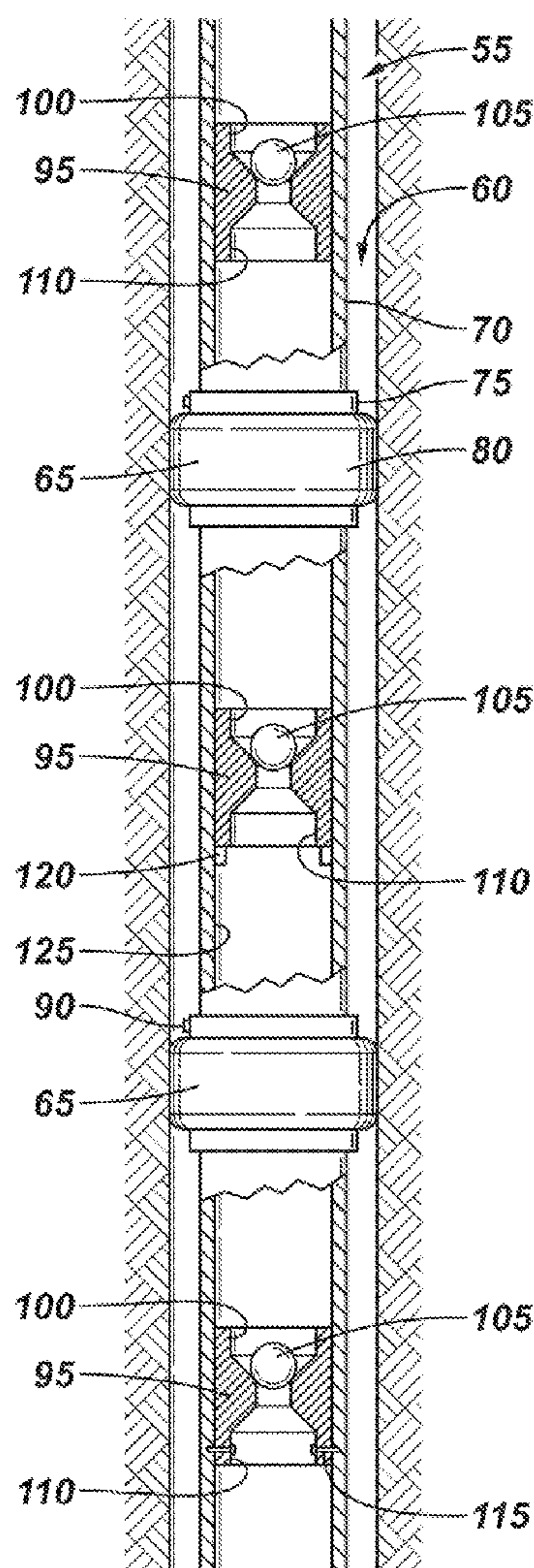
(19) **United States**(12) **Patent Application Publication**
Baihly et al.(10) **Pub. No.: US 2013/0133897 A1**(43) **Pub. Date: May 30, 2013**(54) **MATERIALS WITH ENVIRONMENTAL
DEGRADABILITY, METHODS OF USE AND
MAKING**tinuation-in-part of application No. 11/427,796, filed
on Jun. 30, 2006, now Pat. No. 8,231,947.(75) Inventors: **Jason Baihly**, Katy, TX (US); **Don
Aldridge**, Manvel, TX (US); **Rashmi B.
Bhavsar**, Houston, TX (US); **Manuel P.
Marya**, Sugar Land, TX (US); **Nitin Y.
Vaidya**, Missouri City, TX (US)**Publication Classification**(51) **Int. Cl.**
E21B 34/06 (2006.01)
(52) **U.S. Cl.**
CPC **E21B 34/06** (2013.01)
USPC **166/376; 138/46**(73) Assignee: **SCHLUMBERGER TECHNOLOGY
CORPORATION**, Sugar Land, TX (US)(21) Appl. No.: **13/485,612**(22) Filed: **May 31, 2012**(57) **ABSTRACT****Related U.S. Application Data**(63) Continuation-in-part of application No. 12/371,727,
filed on Feb. 16, 2009, now Pat. No. 8,211,248, Con-A valve device for restricting flow is provided that includes a
degradable portion. A method of temporarily blocking flow is
also provided which includes a degradable portion of an
oilfield element.

FIG. 1

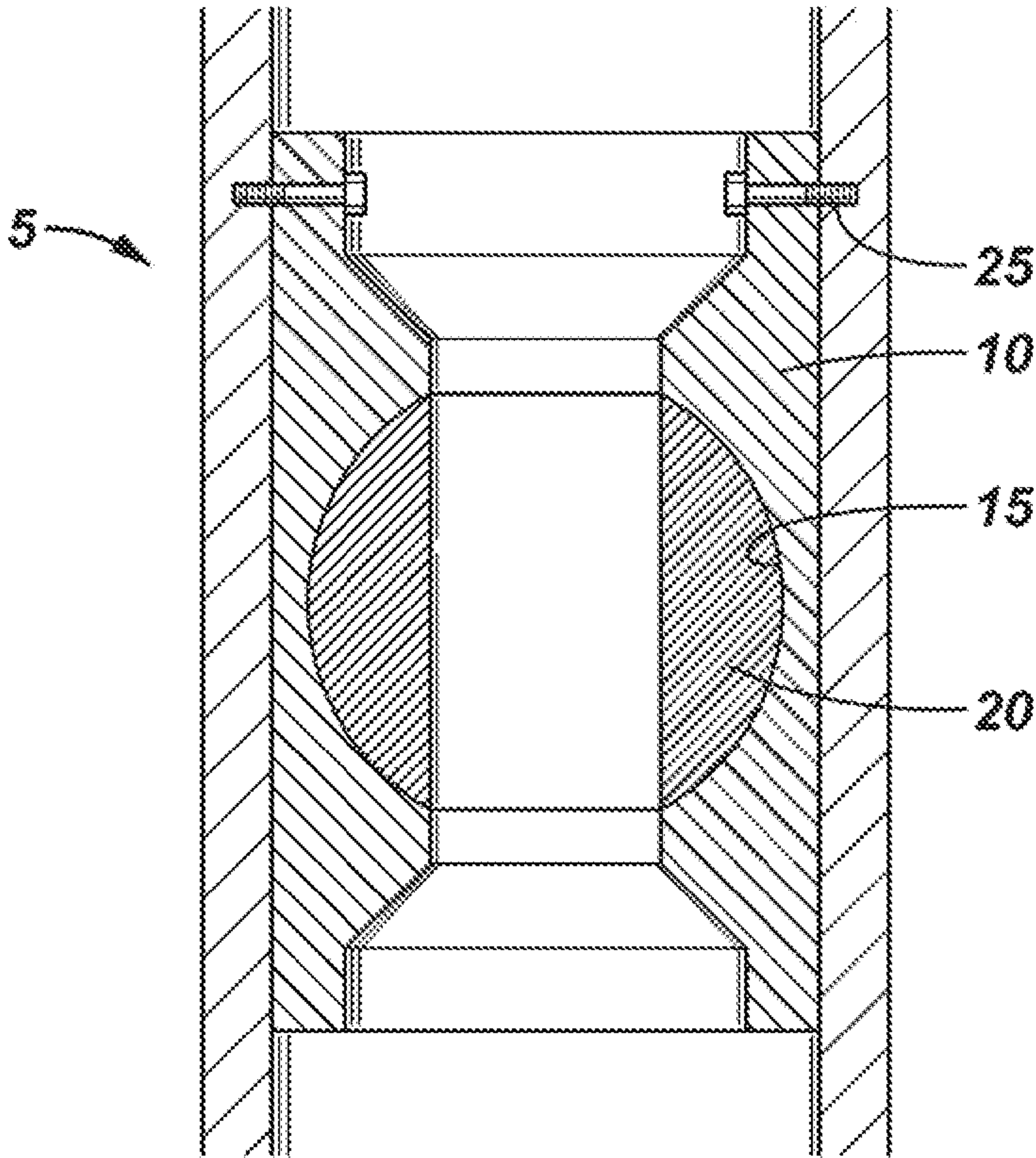


FIG. 2

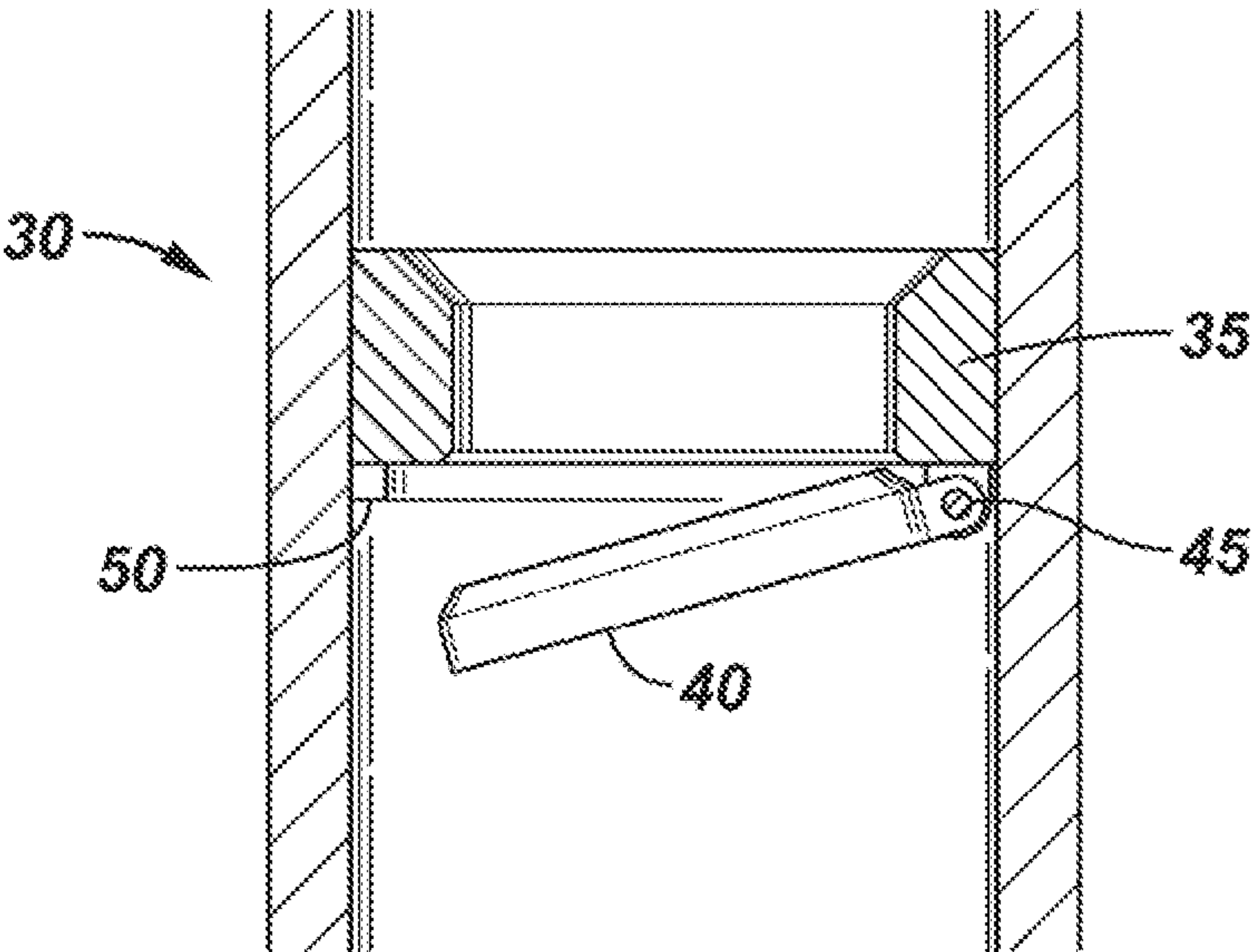
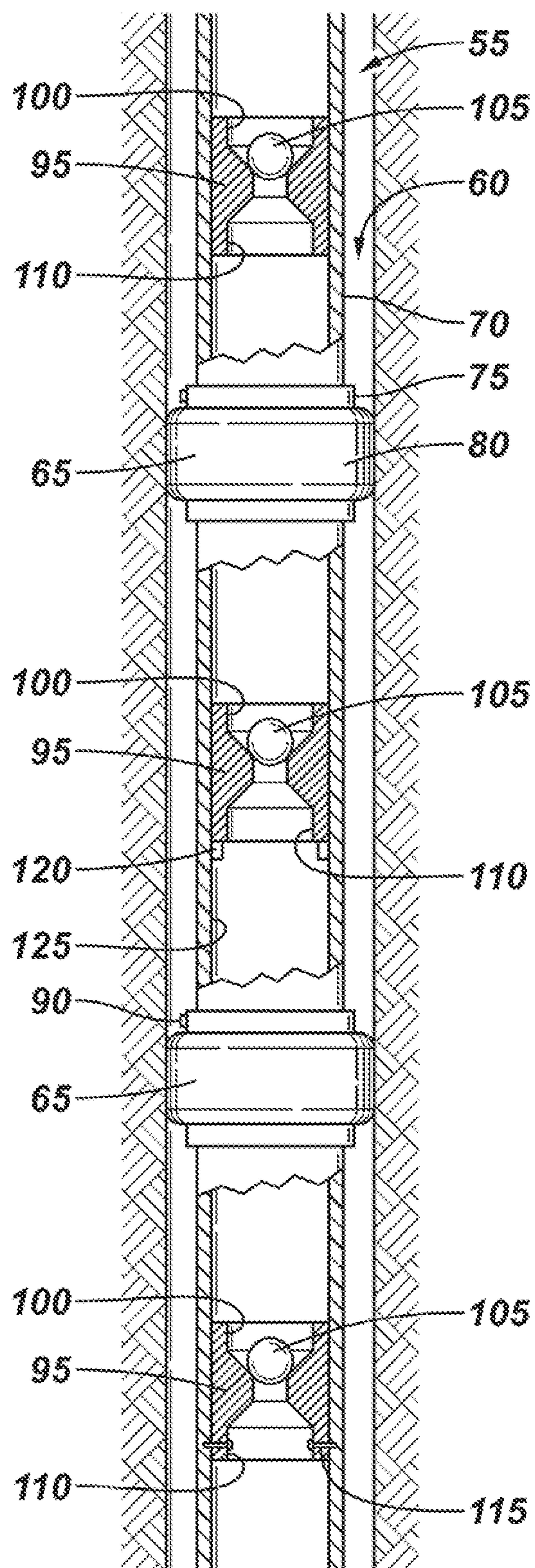


FIG. 3



MATERIALS WITH ENVIRONMENTAL DEGRADABILITY, METHODS OF USE AND MAKING

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] The present application is a continuation-in-part of U.S. Non-Provisional application Ser. No. 12/371,727 filed Feb. 16, 2009, and is a continuation-in-part of U.S. patent application Ser. No. 11/427,796 filed Jun. 30, 2006, both of which are hereby incorporated in their entirety herein.

FIELD

[0002] The invention relates to flow restriction devices and, more particularly, to flow restriction devices having a degradable portion.

BACKGROUND

[0003] Materials that react to external stimuli, for instances changes to their surrounding environments, have been the subject of significant research in view of the potential they offer to sectors of the economy as diverse as the medical, consumer-market, transportation, chemical and petro-chemical sectors. For example, such an advanced material that would have the remarkable ability to degrade in order to actuate a well-defined function as a response to a change in its surrounding may be desirable because no or limited external human intervention would be necessary to actuate the function. Such a material, essentially self-actuated by changes in its surrounding (e.g., the presence or ingress of a specific fluid, or a change in temperature or pressure, among other possible changes) may potentially replace costly and complicated designs and may be most advantageous in situations where accessibility is limited or even considered to be impossible.

[0004] In a variety of subterranean and wellbore environments, such as hydrocarbon exploration and production, water production, carbon sequestration, or geothermal power generation, equipment of all sorts (e.g., subsurface valves, flow controllers, zone-isolation packers, plugs, sliding sleeves, accessories, etc) may be deployed for a multitude of applications, in particular to control or regulate the displacement of subterranean gases and liquids between subsurface zones. Some of these equipments are commonly characterized by relatively complex mechanical designs that are controlled remotely from the rig at ground level via wirelines, hydraulic control lines, or coil tubings.

[0005] Alternatively it may be desirable and economically advantageous to have controls that do not rely on lengthy and costly wirelines, hydraulic control lines, or coil tubings. Furthermore, in countless situations, a subterranean piece of equipment may need to be actuated only once, after which it may no longer present any usefulness, and may even become disadvantageous when for instance the equipment must be retrieved by risky and costly interventions. In such situations, the control or actuation mechanisms may be more conveniently imbedded within the equipment. In other applications, it may be beneficial to utilize the inherent ability of a material for reacting in the presence of an environmental change; for instance such a material may be applied to chemically sense the presence of formation water in a hydrocarbon well. In other foreseen applications, such a degradable material, if complemented by high mechanical strengths, may present

new advantages in aquatic environments not only to withstand elevated differential pressures but also to control equipments deployed underwater with no or limited intervention.

[0006] In some instances, by way of example only, in the petroleum industry, it may be desirable to deploy a piece of equipment, apparatus, or device that performs a pre-determined function under differential pressures and then degrades such that the device no longer requires retrieval or removal by some method. By way of example only it may be advantageous to perform a multiple-stage oilfield operation such as that disclosed in U.S. Pat. No. 6,725,929. However, after the so-called ball, dart or plug is released in the wellbore to block gas and liquid transfers between isolated zones, it may be desirable to remove it by milling, flow-back, or alternate methods of intervention. In some instances, it may be simply more advantageous to manufacture equipments or devices, such as, by way of example only, balls, darts or plugs using a material that is mechanically strong (hard) and degrades under specific conditions, such as in the presence of water-containing fluids like fresh water, seawater, formation water, brines, acids and bases.

[0007] Unfortunately, the degradability of metallic materials, as defined by their lack of stability in a defined environment, as well as their ability to rapidly degrade (as opposed to the slow and uniform rusting or weight loss corrosion of steels for instance) may, in some instances, be accompanied with a number of undesirable characteristics. For example, among the very few metals that react and eventually fully degrade in water, both sodium metal and lithium metal, in addition to having low mechanical strengths, are water-reactive to the point they present great hazard along with great manufacturing, procurement, shipping and, handling challenges. Calcium metal is another reactive metal that in spite of being lesser reactive and slower to react than either sodium or lithium does not possess enough mechanical strength for normal engineering applications. Like sodium metal and lithium metal, calcium metal is thus unfit to many of the pressure-holding applications found for instances in the chemical and petroleum industries. When deficient, the properties of metals may be enhanced by alloying, meaning the chemical mixing of two or more metals and some other substances to form an end product, or alloy, with new properties that may be suitable for practical use. However, the alloying of lithium, sodium, or calcium metals with other metals and substances is not without major metallurgical and manufacturing challenges, and therefore the likelihood of creating an alloy with attractive engineering combinations of high strength, high toughness, and the proper degradability and rate of degradation (in a specific condition) is not only doubtful but also difficult to economically justify.

[0008] Table 1 compares several properties of pure metals with that of exploratory alloys in their annealed conditions (i.e., in the absence of cold working). Are listed in Table 1 measurements of hardness (Vickers hardness, as defined in the ASTM E370 standard) and galvanic corrosion potential, as simply established from voltage average readings of dissimilar metals and alloys electrically coupled by a aqueous electrolyte (here a sodium chloride enriched water). In this document, hardness and microhardness are considered to be fully interchangeable words; i.e., no distinction is made between the two words. Vickers hardness, or Vickers Microhardness, is a well-accepted and straight-forward measure that may be monotonically correlated to the mechanical strength of metals or alloys; e.g., the greater the hardness, the

higher the mechanical strength of the material. Differently, galvanic corrosion potential is an electro-chemical measure of reactivity, more precisely degradability, in an aqueous electrolytic environment, as produced by the coupling of materials with unlike chemical potentials. Though a low galvanic corrosion potential correlates to high degradability in water-containing fluid and often to high rates of degradation, rates of degradation are also influenced by other factors (e.g., water chemistry, temperature, pressure, and anode-to-cathode surface areas). Therefore, simplistically correlating rate of degradation to corrosion potential, despite being macroscopically correct as shown in Table 1, is not fully accurate for materials exhibiting especially comparable corrosion potentials. With these materials, factors such as temperature and water chemistry often have greater impacts on the rates of degradation than the galvanic corrosion potential itself. Galvanic corrosion potential and degradability may be considered purely as thermodynamic quantities, whereas rate of degradation is a kinetic quantity that is also influenced by other factors.

TABLE 1

	Vickers hardness number (HVN)	Galvanic corrosion potential (Volts)*
Aluminum metal (99.99 wt. %)	33.3	-0.60
Magnesium metal (99.99 wt. %)	32.5	-0.90
Calcium metal (99.99 wt. %)	23.1	-1.12
80Al—10Ga—10In **	33.4	-1.48
80Al—5Ga—5Zn—5Bi—5Sn **	33.7	-1.28
75Al—5Ga—5Zn—5Bi—5Sn—5Mg **	40.0	-1.38
65Al—10Ga—10Zn—5Bi—5Sn—5Mg **	39.2	-1.28

*Galvanic corrosion potential was measured against a pure copper electrode (99.99 wt. %) in a 5 percent by eight sodium chloride aqueous solution; i.e., 5 wt. % NaCl in water.

** All alloy compositions are listed in weight percent (wt. %); e.g. 80 wt. % Al—10 wt. % Ga—10 wt. % In.

[0009] Of all aluminum alloys, those referred as the “heat-treatable” alloys exhibit some of the most useful combinations of mechanical strength (hardness), impact toughness, and manufacturability; i.e., the ability to readily make useful articles of manufactures. These alloys are also characterized as being precipitation or age-hardenable because they are hardened or strengthened (the two words are interchangeable) by heat treatments that typically consist of three consecutive steps: (1) a solutionizing (solution annealing) heat-treatment for the dissolution of solid phases in a solid α -aluminum (a refers to pure aluminum’s phase), (2) a quenching or rapid cooling for the development of a supersaturated α -aluminum phase at a given low temperature (e.g., ambient), and (3) an ageing heat treatment for the precipitation either at room temperature (natural aging) or elevated temperature (artificial aging or precipitation heat treatment) of solute atoms within intra-granular phases. During ageing, the solute atoms that were put into solid solution in the α -aluminum phase at the solutionizing temperature and then trapped by the quench are allowed to diffuse and form atomic clusters within the α -aluminum phase. These clusters or ultra fine intra-granular phases result in a highly effective and macroscopic strengthening (hardening) that provides some of the best combinations of mechanical strength and impact toughness.

[0010] An important attribute of age-hardenable alloys is a temperature-dependent equilibrium solid solubility characterized by increasing alloying element solubility with

increasing temperature (up to a temperature above which melting starts). The general requirement for age hardenability of supersaturated solid solutions involves the formation of finely dispersed precipitates during ageing heat treatment. The ageing must be accomplished not only below the so-called equilibrium solvus temperature, but below a metastable miscibility gap often referred as the Guinier-Preston (GP) zone solvus line. For the development of optimal mechanical properties, age-hardening alloys must therefore be heat-treated according to predetermined temperature vs. time cycles. Failures in following an appropriate heat-treatment cycle may result in only limited strengthening (hardening); however any strengthening (hardening) would still be evidence of an ageing response. The presence of age-hardening novel aluminum alloys that possess the unusual ability to degrade in water-containing fluids is a large part of the alloys disclosed herein.

BRIEF DESCRIPTION OF THE FIGURES

[0011] FIG. 1 is a perspective view of a flapper valve;

[0012] FIG. 2 is a side elevational cross sectional view of a ball valve; and

[0013] FIG. 3 is a side elevational view of a tubular within a wellbore.

DETAILED DESCRIPTION

[0014] All alloys shown in Table 2 (including commercially available **6061** alloy) were prepared by induction melting. The alloys were either prepared from commercial alloys, within which alloying elements were introduced from pure metals, or from pure metals. The commercial alloys and the alloying elements were all melted, magnetically, and mechanically stirred in a single refractory crucible. All melts were subsequently poured into 3-in diameter cylindrical stainless steel moulds, resulting in solid ingots weighting approximately 300 grams. The alloy ingots were cross-sections, metallographically examined (results not shown herein), and hardness tested either directly after casting (i.e., in their as-cast condition after the ingots had reached ambient temperature) and/or after ageing heat treatments. The induction furnace was consistently maintained at temperatures below 700° C. (1290° F.) to ensure a rapid melting of all alloying elements but also minimize evaporation losses of volatiles metals such as magnesium. Gaseous argon protection was provided in order to minimize the oxidation of the alloying elements at elevated temperatures and maintain a consistency in the appearance of the cast ingots. All ingots were solidified and cooled at ambient temperature in their stainless steel moulds.

[0015] Solutionizing (solution annealing) was subsequently conducted at 454° C. (850° F.) for 3 hours to create a supersaturated solution. For purposes of simplifications, all alloys were solutionized at this single temperature, even though in reality each alloy has its own and optimal solutionizing (solution annealing) temperature; i.e., each alloy has a unique temperature where solubility of the alloying elements is maximized, and this temperature is normally the preferred solutionizing temperature. Optimal solutionizing (solution annealing) temperatures are not disclosed in this document, as they remain proprietary.

[0016] Immediately after solutionizing (solution annealing), the alloys were oil quenched (fast cooled) to retain their supersaturated state at ambient temperature, and then aged at

170° C. (340° F.) in order to destabilize the supersaturated state and force the formation of a new and harder microstructure with fine precipitates dispersed within an E-aluminum matrix phase. Grain boundary-phase were also observed, but their consequences on alloy properties are not discussed herein, since not relevant to the invention. Vickers microhardness measurements, carried out with 500 g load in accordance with the ASTM E370 standard, were measured at various stages of the ageing heat-treatment all across ingot cross-sections. Though herein are only reported the arithmetic averages of the hardness readings, at least ten microhardness measurements were conducted at each stage of the ageing heat treatment. Hardness was monitored over time for as long as several weeks with the intention to fully replicate the ageing of an alloy in a warm subterranean environment. Hardness vs. time curves were generated to quantify and compare the age-hardening response of the different alloys, as well as the stability of the formed precipitates. FIGS. 1 and 2 compares hardness vs. time responses of 6061 and HT alloy 20, a novel alloy disclosed in Table 2. Despite an evident scatter in the data plotted on FIGS. 1-2 that is characteristic of microstructural imperfections, the novel alloy of FIG. 2 is considerably harder (stronger), exhibiting an average and maximum hardness of about 120 compared to approximately 80 for the cast **6061** alloy in peak-aged condition. Like other well-known age-hardenable alloys, when heat-treated too long at temperatures or over-aged, the novel alloys then experience softening, in stark contrast to the hardening observed earlier during ageing. Rapid decrease in hardness during over-ageing is a direct indication that the formed precipitates are not thermally stable. In stark contrast, stable precipitates, as revealed by no or barely detectable hardness decay over time, may be preferred for most subterranean applications.

[0017] As a substitute to hardness vs. time curves (similar to that of FIGS. 1-2), important hardness results are instead summarized in Table 2 for all 26 novel alloys. Also included in Table 2 are their nominal chemical compositions. For comparison purpose, a 6061 alloy (i.e., a non-degradable and commercially-available aluminum alloy), remelted in the same conditions as the novel alloys is also included in Table 2. Reported in Table 2 are the as-cast hardness (a measure of the hardness after casting and with no subsequent heat-treatment of any sorts) and the peak hardness (i.e., the maximum hardness observed during ageing heat treatment). An increase in hardness from as-cast to aged (heat-treated) conditions is an undeniable proof of age-hardenability.

[0018] In Table 2 the alloys are not categorized in the order they were formulated and thus shaped into ingots; instead they are ranked according to their magnesium content (in percent) to specifically demonstrate the contribution of magnesium as an alloying element. In Table 2, alloying element contents, expressed in percent by weight (wt. %) are as fol-

lows: 0.5 to 8.0 wt. % magnesium (Mg), 0.5 to 8.0 wt. % gallium (Ga), 0 to 2.5 wt. % indium (Ga), 0 to 2.3 wt. % silicon (Si), and 0 to 4.3 wt. % zinc (Zn).

[0019] All alloys were purposely formulated to demonstrate a wide range of magnesium and gallium, along with other alloying elements found in several series of commercial aluminum alloys, among others. FIG. 3, which depicts hardness results from all 26 alloys of Table 2, further reveals that all the novel alloys responded to age-hardening; i.e., they may be strengthened by heat-treatments as are commercial alloys such as the 6061 alloy. While magnesium is known to be an effective solid-solution hardening element that is essential to several commercial alloys, gallium is equally well-known for creating grain-boundary embrittlement by liquation; in other words gallium is known to lower mechanical strength (hardness), specifically by promoting a low-temperature creep-type deformation behavior. In fact in the prior art, gallium—like many low-melting point metals (mercury, tin, lead)—is considered to be detrimental to aluminum; thus gallium like other low-melting point elements is only present in commercial aluminum alloys in impurity levels; removal of these elements even in trace quantities has traditionally been chief in achieving high-quality aluminum alloys for industrial use. FIGS. 4 to 8 confirm that magnesium is also a key contributor in raising hardness in the inventive alloys, either in as-cast or aged condition (heat-treated condition). However, magnesium alone does not suffice to generate an elevated age hardening, unless magnesium is properly combined with gallium, as shown in FIGS. 5 and 8. The data show that hardness values well in excess to that of commercially-available **6061** may be achieved with appropriate combinations of magnesium and gallium (a peak hardness of 140 HVN, well in excess of the measured value in the 80s for the 6061 alloy is reported herein). Not only a maximum hardening occurs at intermediate gallium percentage, as shown in FIG. 5, the ratio of magnesium-to-gallium is also demonstrated to be important. A ratio of in the vicinity of 2 is shown to result in maximum hardness; for practical purposes, magnesium-to-gallium ratios between 0.5 and 3.5 may be recommended to create a variety of mechanical strengths and rates of degradation.

[0020] Furthermore, as pointed out by FIG. 6, silicon (an element essential to alloy 6061 to cause age-hardening) is not seen to influence hardness measurably in any of the novel alloys. Unlike magnesium, zinc (FIG. 7) only appears to slightly reduce hardness, an indication that the addition of zinc in the alloys of this invention interferes with the ageing heat-treatment and the magnesium-gallium alloying. The role of zinc in the novel alloys is thus quite different to that seen in typical commercial aluminum alloys. In many commercial aluminum alloys, zinc is utilized to produce high strength with suitable resistance against corrosion and stress-corrosion cracking.

TABLE 2

	Mg (wt. %)	Ga (wt. %)	In (wt. %)	Si (wt. %)	Zn (wt. %)	Mg/Ga	As-cast HVN	HT to Peak HVN
6061-alloy	1.0	0.0	0.0	0.6	0.1	—	55	78
HT alloy 0	0.5	0.5	0.5	0.0	0.0	1.00	42	78
HT alloy 1	0.5	1.0	1.0	0.0	0.0	0.50	42	78
HT alloy 2	2.0	1.0	1.0	0.0	0.0	2.00	50	90
HT alloy 3	2.1	6.5	2.5	1.1	4.2	0.32	49	75
HT alloy 4	2.2	8.0	2.1	1.1	0.1	0.33	50	85
HT alloy 5	2.2	4.7	0.0	1.1	4.4	0.46	67	97

TABLE 2-continued

	Mg (wt. %)	Ga (wt. %)	In (wt. %)	Si (wt. %)	Zn (wt. %)	Mg/Ga	As-cast HVN	HT to Peak HVN
HT alloy 6	2.2	4.4	1.4	1.1	2.2	0.50	51	88
HT alloy 7	2.2	4.7	1.5	1.1	0.1	0.48	51	89
HT alloy 8	2.3	4.9	0.0	0.5	0.1	0.46	55	104
HT alloy 9	2.3	3.4	1.3	2.3	0.1	0.66	52	100
HT alloy 10	2.3	4.8	0.0	1.4	0.1	0.48	66	100
HT alloy 11	2.3	5.1	0.0	0.6	0.1	0.45	63	107
HT alloy 12	2.3	3.5	1.3	0.6	0.1	0.65	51	96
HT alloy 13	2.3	2.4	0.0	0.6	0.1	0.99	57	94
HT alloy 14	2.4	2.4	0.0	1.2	0.1	0.99	58	91
HT alloy 15	2.4	2.3	0.0	0.6	0.1	1.01	62	100
HT alloy 16	3.5	1.0	1.0	0.0	0.0	3.50	60	99
HT alloy 17	4.3	4.4	0.0	0.5	4.3	0.98	91	125
HT alloy 18	4.4	4.4	1.4	1.1	0.1	1.00	66	104
HT alloy 19	4.4	4.7	0.0	2.2	0.1	0.94	69	108
HT alloy 20	4.5	4.5	0.0	1.1	0.1	1.00	75	123
HT alloy 21	4.5	3.4	1.2	0.5	0.1	1.32	69	125
HT alloy 22	6.2	4.1	1.5	1.2	4.1	1.50	86	111
HT alloy 23	6.6	3.3	1.2	0.5	0.1	1.97	75	143
HT alloy 24	8.0	3.8	1.6	1.2	0.0	2.10	88	132
HT alloy 25	8.0	3.8	1.6	0.0	0.0	2.11	85	136

* HT stands for heat-treatable. HVN stands for Hardness Vickers Number; here measured under a 500 g indentation load.

[0021] Galvanic corrosion potentials of several of the 26 alloys of Table 2 are summarized in Table 3. Galvanic corrosion potential is a valuable indicator of the degradability of the alloy in water-containing environments. Galvanic corrosion potential is here measured by connecting to a voltmeter two electrodes immersed in an electrically conductive 5 wt. % sodium chloride aqueous solution. One electrode is made of one of the test alloys, and the other of a reference material, here selected to be some commercially pure copper (e.g., 99.99% Cu). The voltage, directly read on the voltmeter was determined to be the galvanic corrosion potential. Most generally novel alloys characterized by galvanic corrosion potentials lesser than about -1.2 were observed to exhibit high degradabilities; i.e., they react with the surrounding fluid and produced a characteristic gaseous bubbling. For comparison purposes, galvanic corrosion potentials of magnesium and calcium are shown in Table 1 under the same exact test conditions. Some novel alloys were found to be calcium-like by being highly and rapidly degradable at ambient temperature, while others were found to only rapidly degrade in a calcium-like manner at elevated temperatures and despite the fact that their galvanic corrosion potential is lower than that of either magnesium or calcium. For those alloys not listed in Table 3 but included in Table 2, the measured corrosion potentials were between -1.25 and -1.45 . Generally, the lowest potentials were for those alloys containing indium. It is clear from Table 3 that gallium and indium are both responsible for the degradability of the novel alloys while other elements tend to either enhance or reduce degradability and rates of degradation. With the alloys of this invention, the contribution of gallium is two-fold: gallium increases both hardness (strength) and degradability.

TABLE 3

	As-cast (V)	HT to Peak (V)
Cast 6061	-0.60	-0.60
HT alloy 4	-1.47	-1.42
HT alloy 5	-1.30	-1.31
HT alloy 7	-1.42	-1.41

TABLE 3-continued

	As-cast (V)	HT to Peak (V)
HT alloy 8	-1.30	-1.30
HT alloy 10	-1.28	-1.35
HT alloy 11 [†]	-1.32	-1.29
HT alloy 13	-1.28	-1.27
HT alloy 14	-1.28	-1.32
HT alloy 15	-1.30	-1.32
HT alloy 19	-1.29	-1.36
HT alloy 20*	-1.31	-1.32

[†]Galvanic corrosion potential was found to increase slightly as bubbling proceeded.

*Galvanic corrosion potential was unstable, thus making the measurement unreliable.

[0022] Another type of material useful in forming oilfield elements comprises a combination of normally insoluble metal or alloys with metallurgically-soluble (partially/wholly) and/or blendable elements selected from other metals or alloys, semi-metallic elements, and/or non-metallic elements; thus new compositions to form new complex alloys and composite structures of poor stability in the designated fluid environment. Examples of metals preferentially selected to develop high strength include iron, titanium, copper, combinations of these, and the like, among other metals. Second metals, semi-metallic elements, and non-metallic elements contemplated are any metal, semi-metallic element, or non-metallic element that will form a non-durable (degradable) composition with the first element. Examples include metals such as gallium, indium, tin, antimony, combinations of these, and the like; semi-metallic elements such as carboxylated carbon (e.g. in graphitic or nanotube form), and organic compounds such as sulfonated polystyrene, styrene sulfonic acid, and compositions comprising non-metallic materials such as oxides (anhydride), carbonates, sulfides, chlorides, bromides, acid-producing or basic producing polymers, or in general fluid pH changing polymers. Many of these non-metallic materials may contain metals that are chemically-bonded to non-metallic elements (wherein the bonds may be ionic, covalent, or any degree thereof). These materials include, but are not limited to, alkaline and alkaline-earth oxides, sulfides, chlorides, bromides, and the like. These

materials, alone, are at least partially water-soluble and, when properly combined (e.g. blended) with normally insoluble metals and alloys, will degrade the chemical resistance of the normally insoluble metals by changing the designated fluid chemistry, including its corrosiveness, thus creating galvanic cells, among other possible mechanisms of degradations. Examples of normally insoluble metals and alloys made soluble through the additions of elements, including polymers, that would directly destabilize the metallic state of the normally insoluble element for a soluble ionic state (e.g. galvanic corrosion, lower pH created by acid-polymers), or indirectly by promoting ionic compounds such as hydroxides, known to predictably dissolve in the designated fluid environment. Also contemplated are exothermic reactions occurring in fluid such as water that may act as trigger to the degradation of one of the composition. The ratio of normally insoluble metal to metallurgically soluble or blendable elements is dependent on the end use of the oilfield element, the pressure, temperature, and element lifetime requirements as well as the fluid environment compositions, and, without limiting the applications, may range from 4:1 to 1:1 for instance.

[0023] Another group of materials useful in oilfield elements includes one or more solubility-modified high strength and/or high-toughness polymeric materials that may be selected from polyamides (including but not limited to aromatic polyamides), polyethers, and liquid crystal polymers. As used herein, the term “polyamide” denotes a macromolecule containing a plurality of amide groups, i.e., groups of the formula —NH—C(=O)— and/or —C(=O)—NH— . Polyamides as a class of polymer are well known in the chemical arts, and are commonly prepared via a condensation polymerization process whereby diamines are reacted with dicarboxylic acid (diacids). Copolymers of polyamides and polyethers may also be used, and may be prepared by reacting diamines with diacids.

[0024] Useful aromatic polyamides include those generically known as aramids. Aramids are highly aromatic polyamides characterized by their flame retardant properties and high strength. They have been used in protective clothing, dust-filter bags, tire cord, and bullet-resistant structures. They may be derived from reaction of aromatic diamines, such as para- and/or meta-phenylenediamine, and a second monomer, such as terephthaloyl chloride.

[0025] Polyethers as a class of polymer are also well known, where one type of polyether is commonly prepared by reaction of an alkylene oxide (e.g., ethylene oxide) with an initiating group (e.g., methanol). The term “polyether” as used herein denotes a macromolecule containing a plurality of ether groups, i.e., groups of the formula R—O—R where R represents an organic (carbon-containing) group. At present, many polyethers are commercially available that have terminating groups selected from amine, hydroxyl and carboxylic acid. Polyethers having two amine terminating groups may be used according to U.S. Pat. No. 6,956,099, incorporated herein by reference, to introduce polyether blocks into a polyamide copolymer. This approach provides blocks of polyether groups within a polyamide copolymer.

[0026] As noted in U.S. Pat. No. 5,057,600, incorporated herein by reference, “poly(etheretherketone)” or “PEEK” refers to a polymeric material which comprises poly(etheretherketone), i.e., [poly(oxy-p-phenyleneoxy-p-phenylene-carbonyl-p-phenylene)]. PEEK is a widely available semi-crystalline or amorphous high performance thermoplastic

polymeric material. PEEK is soluble in only a few solvents. Some of the solvents require high temperatures while other solvents such as sulfuric acid, sulfonate the PEEK molecules, which alters the polymer and complicates characterization. Solution properties of PEEK have been studied by Berk, C. and Berry, G. C., *J. Polym. Sci.: Part B: Polym. Phys.*, 28, 1873 (1990); Bishop et al., *Macromolecules*, 18, 86 (1985); Roovers et al., *Macromolecules*, 26, 3826 (1993); and Roovers, et al., *Macromolecules*, 23, 1611 (1990).

[0027] Other similar polymeric (PEEK-type polymers) materials such as poly(aryletherketone) (PAEK), poly(etherketone) (PEK), or poly(etherketoneketone) (PEKK), may also be polymers. Further, poly(etheretheretherketone) (PEEEK), poly(etheretherketoneetherketone) (PEEKEK), poly(etheretherketoneketone) (PEEKK), poly etherketoneetherketoneketone) (PEKEKK) are also to be considered as PEEK-type polymers, both individually and as mixtures and as copolymers with each other. Polymer mixtures of these PEEK-type polymers with poly(phenylene sulfide) or “PPS” are also.

[0028] Other degradable materials include those described in U.S. patent application Ser. No. 11/162,184 filed Aug. 31, 2005, and U.S. patent application Ser. No. 11/427,233, filed Jun. 28, 2006, all of which are incorporated by reference in their entirety herein.

[0029] Although the alloys and other materials disclosed and claimed herein are not limited in utility to oilfield applications (but instead may find utility in many applications in which hardness (strength) and degradability in a water-containing environment are desired), it is envisioned that the alloys and other materials disclosed and claimed herein will have utility in the manufacture of oilfield devices. For example, the manufacture of plugs, valves, sleeves, sensors, temporary protective elements, chemical-release devices, encapsulations, and even proppants. Additionally, oilfield devices include, but is not limited to one or more items or assemblies selected from tubing, blow out preventers, sucker rods, O-rings, T-rings, jointed pipe, electric submersible pumps, packers, centralizers, hangers, plugs, plug catchers, check valves, universal valves, spotting valves, differential valves, circulation valves, equalizing valves, safety valves, fluid flow control valves, connectors, disconnect tools, down-hole filters, motorheads, retrieval and fishing tools, bottom hole assemblies, seal assemblies, snap latch assemblies, anchor latch assemblies, shear-type anchor latch assemblies, no-go locators, and the like. These oilfield devices can be used in a number of well operations, including fracturing and stimulation operations.

[0030] Well operations include, but are not limited to, well stimulation operations, such as hydraulic fracturing, acidizing, acid fracturing, fracture acidizing, or any other well treatment, whether or not performed to restore or enhance the productivity of a well. Stimulation treatments fall into two main groups, hydraulic fracturing treatments and matrix treatments. Fracturing treatments are performed above the fracture pressure of the reservoir formation and create a highly conductive flow path between the reservoir and the wellbore. Matrix treatments are performed below the reservoir fracture pressure and generally are designed to restore the natural permeability of the reservoir following damage to the near-wellbore area.

[0031] Hydraulic fracturing, in the context of well workover and intervention operations, is a stimulation treatment routinely performed on oil and gas wells in low-permeability

reservoirs. Specially engineered fluids are pumped at high pressure and rate into the reservoir interval to be treated, causing a vertical fracture to open. The wings of the fracture extend away from the wellbore in opposing directions according to the natural stresses within the formation. Proppant, such as grains of sand of a particular size, is mixed with the treatment fluid keep the fracture open when the treatment is complete. Hydraulic fracturing creates high-conductivity communication with a large area of formation and bypasses any damage that may exist in the near-wellbore area.

[0032] In the context of well testing, hydraulic fracturing means the process of pumping into a closed wellbore with powerful hydraulic pumps to create enough downhole pressure to crack or fracture the formation. This allows injection of proppant into the formation, thereby creating a plane of high-permeability sand through which fluids can flow. The proppant remains in place once the hydraulic pressure is removed and therefore props open the fracture and enhances flow into the wellbore.

[0033] Acidizing means the pumping of acid into the wellbore to remove near-well formation damage and other damaging substances. This procedure commonly enhances production by increasing the effective well radius. When performed at pressures above the pressure required to fracture the formation, the procedure is often referred to as acid fracturing. Fracture acidizing is a procedure for production enhancement, in which acid, usually hydrochloric (HCl), is injected into a carbonate formation at a pressure above the formation-fracturing pressure. Flowing acid tends to etch the fracture faces in a non-uniform pattern, forming conductive channels that remain open without a propping agent after the fracture closes. The length of the etched fracture limits the effectiveness of an acid-fracture treatment. The fracture length depends on acid leakoff and acid spending. If acid fluid-loss characteristics are poor, excessive leakoff will terminate fracture extension. Similarly, if the acid spends too rapidly, the etched portion of the fracture will be too short. The major problem in fracture acidizing is the development of wormholes in the fracture face; these wormholes increase the reactive surface area and cause excessive leakoff and rapid spending of the acid. To some extent, this problem can be overcome by using inert fluid-loss additives to bridge wormholes or by using viscosified acids. Fracture acidizing is also called acid fracturing or acid-fracture treatment.

[0034] A “wellbore” may be any type of well, including, but not limited to, a producing well, a non-producing well, an injection well, a fluid disposal well, an experimental well, an exploratory well, and the like. Wellbores may be vertical, horizontal, deviated some angle between vertical and horizontal, and combinations thereof, for example a vertical well with a non-vertical component.

[0035] In addition, it may be desirable to use more than one material as disclosed herein in an apparatus. It may also be desirable in some instances to coat the apparatus comprising the degradable material with a material which will delay the contact between the water-containing atmosphere and the degradable material. For example, a plug, dart or ball for subterranean use may be coated with thin plastic layers or degradable polymers to ensure that it does not begin to degrade immediately upon introduction to the water-containing environment. As used herein, the term degrade means any instance in which the integrity of the material is compromised and it fails to serve its purpose. For example, degrading

includes, but is not necessarily limited to, dissolving, partial or complete dissolution, or breaking apart into multiple pieces.

[0036] FIGS. 1 and 2 are exemplary valves with which the degradable material may be utilized. As shown in FIG. 1, a ball valve mechanism 5 can include a body 10, a seat portion 15 and a ball portion 20. The ball valve mechanism 5 can be secured by a securing mechanism 25, such as a bolt, or the ball valve mechanism 5 can be held in place by an external support, such as a shelf or lip on the inner surface of a tubular member. Any or all of the ball valve mechanism 5 can be constructed from a degradable material, including but not limited to the body 10, seat portion 15, ball portion 20 and the securing mechanism 25, so long that as a result of the degradation, a flow path is opened past the location at which the valve 5 was positioned.

[0037] Similar to FIG. 1, the flapper valve 30 detailed in FIG. 2 can include a valve body 35, a flapper portion 40 and a hinge connection mechanism 45 between the valve body 35 and flapper portion 40. Similar to the ball valve mechanism 5, the flapper valve 30 can be secured by a securing mechanism, such as a bolt, or the flapper valve mechanism 30 can be held in place by an external support 50, such as a shelf or lip on the inner surface of a tubular member. Any or all of the flapper valve mechanism 30 can be constructed from a degradable material, including but not limited to the body 35, flapper portion 40 and the external support 50, a flow path is opened past the location at which the valve 30 was positioned.

[0038] FIG. 3 illustrates a tubular string 55 positioned within a wellbore 60. A series of packers 65 are positioned within the annulus about the outer surface 70 of the tubular string 55 and include a metal frame portion 75 and a sealing portion 80 which engages the wall 85 of the wellbore 60. The metal frame portion 75 of the packers 65 can be formed of a degradable material so that, as the frame portion 75 degrades, the packer 65 comes free from the tubular string 55 and can drop down the wellbore 60. Alternatively, a securing mechanism 90, such as a bolt, connecting the packer 65 to the outer surface 70 of the tubular string 55 can be formed of a degradable material so that, as the securing mechanism 90 degrades, the packer 65 is no longer secured to the tubular string 55. Other oilfield elements known to be positionable within the annulus, such as a slip, can further be constructed to include a degradable material so that, upon degradation of the material, a flow path is formed therepast or the oilfield element can drop away from the tubular to a position downhole.

[0039] Within the tubular string 55 are a series of seat members 95. The seat members 95 include an upwardly facing concave portion 100 to receive a dropped element 105, such as a ball, therein to provide a fluid barrier. As shown, the seat members 95 can further include a downwardly, facing concave portion 110 which can also be configured to provide a fluid barrier. As shown in FIG. 3, the seat members 95 can be secured to the tubular string 55 by a securing mechanism 115, such as a bolt. Alternatively, for example, the seat members 95 can be placed on a ledge 120 extending from an inner surface 125 of the tubular string 55. The dropped element 105 can be formed of a degradable material so that, as the dropped element 105 degrades, the flow path through the seat member 95 is reopened. Additionally, the seat member 95 can be completely or partially formed of a degradable material, the securing mechanism 115 can be formed of a degradable mate-

rial, and/or the ledge **120** extending from the inner surface **125** of the tubular string **55** can be formed of a degradable material.

[0040] In addition to the oilfield elements described above, it is contemplated that valves, plugs, balls, seats and other oilfield elements made of a degradable material can be situated to block flow toward the surface until degradation occurs. In particular, these oilfield elements can be configured to block flow from a formation to a position uphole.

[0041] Certain embodiments and features have been described using a set of numerical upper limits and a set of numerical lower limits. It should be appreciated that ranges from any lower limit to any upper limit are contemplated unless otherwise indicated. Certain lower limits, upper limits and ranges appear in one or more claims below. All numerical values are “about” or “approximately” the indicated value, and take into account experimental error and variations that would be expected by a person having ordinary skill in the art.

[0042] Various terms have been defined above. To the extent a term used in a claim is not defined above, it should be given the broadest definition persons in the pertinent art have given that term as reflected in at least one printed publication or issued patent. Furthermore, all patents, test procedures, and other documents cited in this application are fully incorporated by reference to the extent such disclosure is not inconsistent with this application and for all jurisdictions in which such incorporation is permitted.

[0043] While the foregoing is directed to embodiments of the present invention, other and further embodiments of the invention may be devised without departing from the basic scope thereof, and the scope thereof is determined by the claims that follow.

What is claimed is:

1. A valve device for at least partially obstructing flow, the valve device comprising:

- a valve body portion;
- a securing portion of the valve body portion configured to securely position the valve body portion in a predetermined location;
- a valve seat portion of the valve body portion;
- an obstructing portion configured to engage against the valve seat portion and restrict flow therepast; and
- a degradable portion of the valve body portion configured to degrade when exposed to specific environmental conditions.

2. The valve device of claim **1**, wherein the degradable portion includes the valve body portion.

3. The valve device of claim **2**, wherein the degradable portion further includes the obstructing portion.

4. The valve device of claim **1**, wherein the degradable portion includes the securing portion so that, upon degradation thereof, the valve body portion is no longer secured in the predetermined location.

5. The valve device of claim **4**, wherein the securing portion is a bolt member.

6. The valve device of claim **1**, wherein the degradable portion comprises aluminum.

7. The valve device of claim **6**, wherein the degradable portion comprises magnesium.

8. The valve device of claim **6**, wherein the degradable portion comprises zinc.

9. The valve device of claim **6**, wherein the degradable portion comprises a non-metal.

10. A method of temporarily blocking flow in a well bore, the method comprising:

- positioning an oilfield element in a wellbore to block fluid flow therepast;
- exposing the oilfield element to a wellbore condition; and
- degrading a degradable portion of the oilfield element so as to allow fluid flow to resume therepast.

11. The method of claim **10**, wherein positioning an oilfield element in a wellbore to block fluid flow therepast includes positioning a valve body portion of a valve device within a wellbore, the valve body portion having a valve seat portion; placing a blocking portion of the valve device in the wellbore configured to engage the valve seat portion and block fluid therepast; and

- engaging the valve seat portion of the valve body portion with the blocking portion to block fluid flow therepast.

12. The method of claim **11**, wherein the blocking portion is a ball.

13. The method of claim **11**, wherein the degradable portion of the oilfield element is the valve device.

14. The method of claim **11**, wherein the degradable portion of the oilfield element is the valve seat portion.

15. The method of claim **11**, wherein the degradable portion of the oilfield element is the valve body portion.

16. The method of claim **11**, wherein the degradable portion is an engaging portion of the valve body portion configured to secure the valve body portion within the wellbore.

17. The method of claim **10**, including releasing a chemical from the degradable portion upon the degradation thereof.

18. The method of claim **17**, wherein the chemical released from the degradable portion is selected to provide an identifiable signature within the wellbore fluids detectable by a downhole sensor.

19. The method of claim **17** including verifying degradation of the degradable portion by the downhole sensor.

20. The method of claim **10**, wherein the oilfield element is a packer.

* * * * *