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(71) Applicant *(for all designated States except US)*: E-CELL CORPORATION [CA/CA]; 52 Royal Road, Guelph, Ontario N1H 1G3 (CA).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: TESSIER, David, Florian [CA/CA]; 510–244 Willow Road, Guelph, Ontario N1H 6R5 (CA). KOSIR, Tom [CA/CA]; Apartment 703, 2435 Second Street, Burlington, Ontario L7R 1E5 (CA). SIVERNS, Steve [CA/CA]; 98 Oak Knoll Drive, Hamilton, Ontario L8S 4C5 (CA). HUEHNERGARD, Mark, Philip [CA/CA]; 21 Springdale Drive, Kitchener, Ontario N2K 1P8 (CA). GLEGG, Robert [CA/CA]; 250 Boland Crescent, Campbellville, Ontario L0P 1B0 (CA).

(74) Agent: FORS, Arne, I.; Gowling, Strathy & Henderson, Suite 4900, Commerce Court West, Toronto, Ontario M5L 1J3 (CA).

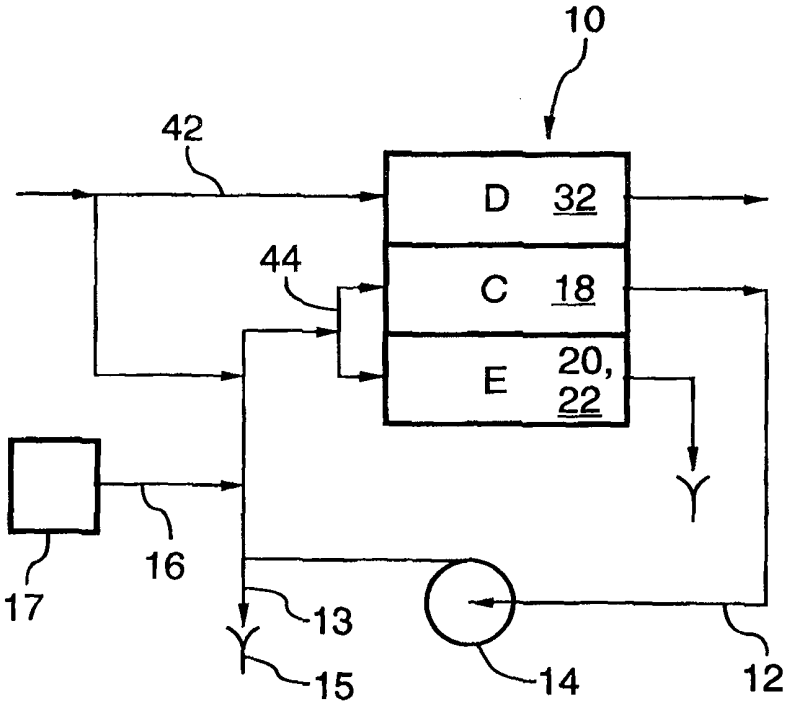
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(54) Title: METHOD FOR REDUCING SCALING IN ELECTRODEIONIZATION SYSTEMS

(57) Abstract

A method and apparatus for inhibiting scaling in an electrodeionization system (10) or in a combined reverse osmosis/electrodeionization system (62, 10) for water treatment and, more particularly, for increasing tolerance to hardness in the feed water to an electrodeionization unit (10) to inhibit precipitation of metal cations contained in the feed water and for increasing efficiency of the electrodeionization system. Water to be purified is passed through an electrodeionization unit (10) in which a concentrate stream recycling (12) through concentrating compartments (18) and anode and cathode compartments (20, 22) contains effective amounts of an antiscalant to inhibit precipitation of scale. One or more preliminary reverse osmosis units (62, 72, 74, 90, 100, 110, 120, 130, 140) in series with the electrodeionization unit (10) preferably receives a portion of the antiscalants in the concentrate stream (12, 44). The antiscalant in the water fed to the reverse osmosis unit (62) can be supplemented and adjusted. Electrolyte can be provided to the concentrate stream (44) of the electrodeionization unit from products of the reverse osmosis.



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METHOD FOR REDUCING SCALING IN ELECTRODEIONIZATION SYSTEMS

BACKGROUND OF THE INVENTION

(i) Field of the Invention

The present invention relates to a method and apparatus for inhibiting scaling in an electrodeionization system or in a combined reverse osmosis/electrodeionization system for water treatment and, more particularly, for increasing tolerance to hardness in the feed water to an electrodeionization unit to inhibit precipitation of metal cations contained in the feed water and for increasing efficiency of the electrodeionization system.

(ii) Description of the Related Art

The purification of liquid has become of great interest in many industries. In particular, pure water is used for many industrial purposes such as, in processes for producing semiconductor chips, in power plants, in the petro chemical industry and for many other purposes.

Ion exchange resins, reverse osmosis filtration and electrodialysis techniques have been used to reduce the concentration of ions in a liquid.

Electrodeionization apparatus have recently been used with more frequency to reduce the concentration of ions in a liquid. The term "electrodeionization" generally refers to an apparatus and a process for purifying liquids which combine ion exchange resins, ion exchange membranes and electricity to purify the liquids. An

electrodeionization module comprises alternating arrangements of cation permeable membranes and anion permeable membranes defining compartments therebetween. In alternating compartments, there is provided ion exchange resin beads. Those compartments are known as diluting compartments. The compartments which generally do not contain ion exchange resin are known as the concentrating compartments. Ions migrate from the diluting compartments through ion exchange beads and ion permeable membranes into the concentrating compartments by the introduction of current. The liquid flowing through the concentrating compartments is discarded or partially recycled and the purified liquid flowing through the diluting compartments is recovered as demineralized liquid product.

Scaling of electrodeionization equipment is of particular concern as it reduces membrane efficiencies and fouls electrode surfaces. Scaling has been found to occur in localized regions of electrodeionization equipment, and particularly those where high pH is typically present. Such regions include those on the surface of the concentrate-chamber side of anion exchange membranes, due to the flux of hydroxyl ions resulting from the regenerative water splitting process in the diluting chambers. Localized regions of high pH are also typically present on the cathode surface due to the evolution of hydrogen gas and concomitant production of hydroxyl ion according to the cathodic electrode reaction:

$$2e- + 2H_2O = H_2\ (gas) + 2OH-$$

These localized regions of high pH provide conditions under which scales harmful to the performance of the electrodeionization device can form. Generally, these scales form in the presence of polyvalent metal cations such as Ca^{2+}, Mg^{2+}, Sr^{2+}, Ba^{2+}, Fe^{3+}, Al^{3+}

and the like which can precipitate under local high pH conditions as hydroxides, sulphates, phosphates, oxides and carbonates, when carbonate, bicarbonate or carbon dioxide are present and as mixed oxides such as spinels, mixed carbonates and fluorides, when fluoride ions are present. Due to the low solubility products of these compounds, even trace amounts of these metal cations and counter anions in the concentrate streams will be sufficient to cause undesirable precipitation.

In reverse osmosis, as water passes through the membrane driven by the pressure difference between concentrate and permeate streams, the concentrate stream becomes progressively more concentrated and the solubility limit of salts of the dissolved ions can be exceeded, leading to precipitation of $CaCO_3$ and other solids as scale. This mechanism of scale formation is fundamentally different from that in electrodeionization where the anion membranes surfaces (concentrate side) are actively maintained at a high pH due to the migration of hydroxyl ions from water splitting in the diluting chambers.

Antiscalants are used to prevent growth of such scales. These act by a number of mechanisms, including: a) inhibiting the nucleation of scale particles, usually with a sub-stoichiometric amount of antiscalant compared with scale forming ions; b) inhibiting the growth of scale particles, usually with a sub-stoichiometric amount of antiscalant compared with scale forming ions; c) solution complexing of the ions of the scale, thereby lowering the thermodynamic tendency (Gibbs energy change) for scale to form, and usually using a stoichiometric amount of antiscalant (chelating agent) compared with scale forming ions. Due to the relatively high concentration of ions in typical reverse osmosis feed water, effects a) and b) are usually effected by the introduction of antiscalant to the reverse osmosis feed. Lowering of the reverse osmosis feed pH is also

commonly practised. The net effect is to permit operation of reverse osmosis systems at higher recovery than otherwise possible.

Although it is known to add antiscalants to reverse osmosis, it is not conventional practice to add antiscalants to electrodeionization cells for reducing scale formation. A paper entitled Studies on Polarity Reversal with Continuous Deionization by Yoram Oren et al. published in Desalination, 86 (1992) 155 - 172 by Elsevier Science Publishers B.V., Amsterdam, states that scale formation in continuous deionization, i.e., electrodeionization, can be minimized by reducing the concentration of calcium and magnesium (softening) or acidification which reduces pH in sensitive areas, or addition of antiscalants to form complexes with the calcium or magnesium ions or to delay precipitation. However, it is further stated that all such solutions add undesirable chemicals to the water and require equipment to introduce the chemicals.

Summary of The Invention

In its broad aspect, the method of the invention for inhibiting formation of scale in an electrodeionization unit for deionizing water having an anode compartment at one end of the unit, a cathode compartment at the opposite end of the unit, and a plurality of diluting compartments alternating with concentrating compartments positioned between the said anode and cathode compartments comprises passing feed water to be deionized through the diluting compartments; passing water or an aqueous solution for accepting ions from the feed water through the concentrating compartments, and through the anode and cathode compartments; applying an electrical voltage between the said anode and the said cathode whereby ions in the feed water migrate to the water or aqueous solution in

the concentrating compartments; collecting and discharging aqueous solution from the anode and cathode compartments; recycling water or aqueous solution from the concentrating compartments as a concentrate stream through the concentrating compartments and through the anode and cathode compartments; and injecting an antiscalant to the concentrate stream recycling through the concentrating compartments and through the anode and cathode compartments in an amount effective to inhibit scale formation in the concentrating compartments and in the cathode compartment. The effective amount of antiscalant in the concentrate stream is in the range of 1 to 400 ppm, and may be selected from the group consisting of sulphuric acid, hydrochloric acid, polyacrylic acid, derivatives of polyacrylic acids co-polymerized with sulfonates, phosphonate-type antiscalants, sodium hexametaphosphate, EDTA and CDTA complexing agents, amido succinic acid chelating agent, non-oxidizing biocidal agents typified by sodium bisulphite, and combinations thereof.

In a preferred aspect of the invention, the method for purifying and deionizing water for inhibiting formation of scale in a reverse osmosis in an electrodeionization unit in series in which water to be purified and deionized passes through the reverse osmosis unit to produce a permeate stream and a retentate discharge stream, and in which the electrodeionization unit has an anode compartment at one end of the unit, a cathode compartment at the opposite end of the unit, and a plurality of diluting compartments alternating with concentrating compartments positioned between the said anode and cathode compartments, comprises passing feed water to be purified and deionized through the reverse osmosis unit; passing permeate from the reverse osmosis unit through the diluting compartmetns of the deionization unit; passing water or an aqueous solution

for accepting ions from the feed water through the concentrating compartments, and through the anode and cathode compartments; applying an electrical voltage between the said anode and the said cathode whereby ions in the feed water migrate to the water or aqueous solution in the concentrating compartments; collecting and discharging aqueous solution from the anode and cathode compartments; recycling water or aqueous solution from the concentrating compartments as a concentrate stream through the concentrating compartments and through the anode and cathode compartments; injecting an antiscalant to the concentrate stream recycling through the concentrating compartments and through the anode and cathode compartments effective to inhibit scale formation in the concentrating compartments and in the cathode compartment; bleeding a portion of the concentrate stream containing antiscalant; and combining and passing said portion of the bled concentrate containing an amount of antiscalant with the feed water through the reverse osmosis unit, adjusting the amount of antiscalant in the water to the reverse osmosis unit to provide an effective amount of antiscalant to inhibit scale formation in the reverse osmosis unit, and passing the permeate stream through the dilute compartments of the deionization unit.

The feed water can be subjected to reverse osmosis in a plurality of passes, each pass comprising one or more stages, wherein permeate from at least one of the stages or one of the passes is combined with the concentrate stream for passage through the concentrating compartments and through the anode and cathode compartments to add electrolyte thereto, thereby increasing electrical conductivity. The retentate from at least one of the stages, excepting from the first reverse osmosis pass, can be combined with the concentrate stream for passage through the concentrating compartments. The

antiscalant can be sulphuric acid in the range of about 500 to 0.5 ppm, hydrochloric acid in the range of about 365 to about 0.4 ppm or sodium hexametaphosphate in an amount in the range of about 5 to about 200 ppm, preferably about 25 to about 100 ppm.

The antiscalant in the water to the reverse osmosis unit preferably is adjusted to an amount in the range of 1 to 75 ppm effective to inhibit scaling therein.

In a further embodiment of the invention, a portion of the permeate is added to the concentrate stream passing through the concentrating compartments and through the anode and cathode compartments to provide electrolyte thereto, whereby electrical conductivity is increased.

Brief Description of The Drawings

The method and apparatus of the invention will now be described with reference to the accompanying drawings, in which:

Figure 1 is a schematic flowsheet of a first embodiment of the present invention;

Figure 2 is a schematic drawing of an electrodeionization unit of the present invention embodying the embodiment shown in Figure 1;

Figure 3 is a schematic flowsheet of a second embodiment of the present invention in conjunction with the embodiment shown in Figure 1;

Figure 4 is a schematic flowsheet of a third embodiment of the present invention in conjunction with the embodiment shown in Figure 1;

Figure 5 is a schematic flowsheet of a fourth embodiment of the present invention in conjunction with the embodiment shown in Figure 1; and

Figure 6 is a schematic flowsheet of a fifth embodiment of the present invention

in conjunction with the embodiment shown in Figure 1.

Description of the Preferred Embodiment

The processes of the present invention will be described with reference to the accompanying drawings. In general, the invention is applicable to water purification processes which are carried out using an electrodeionization unit or with an electrodeionization unit and reverse osmosis unit in series.

Referring first to Figure **1**, the embodiment of the present invention illustrated comprises a process for purifying water including an electrodeionization unit **10,** a recirculation loop **12** having pump **14** for recycle of concentrate solution, a concentrate bleed line **13** to drain **15**, and an injection line **16** for injecting antiscalants acids from injection unit **17** into the concentrate compartments **18** and the anode and cathode compartments **20** and **22** respectively.

Referring now to Figure **2**, the electrodeionization unit **10** in accordance with the present invention, described in more detail, comprises the anode compartment **20** provided with an anode **24** and the cathode compartment **22** provided with a cathode **26**. A plurality of cation exchange membranes **28** and anion exchange membranes **30** are alternately arranged between the anode compartment **20** and the cathode compartment **22** to form diluting compartments **32** each defined by anion exchange membrane **30** on the anode side and by a cation exchange membrane **28** on the cathode side and concentrating compartments **18** each defined by a cation exchange membrane **28** on the anode side and by an anion exchange membrane **30** on the cathode side. Electrolyte solution is supplied to anode compartment **20** and to cathode compartment **22** via

flowstreams **36** and **38** respectively.

Ion exchange material such as ion exchange resin beads designated by numeral **40** preferably are provided in diluting compartments **32**. These may comprise either anion or cation exchange resins or a mixture thereof, mixed bed, layers, continuous/discontinuous phases, and the like, such as disclosed in PCT Application No. Serial No. PCT/CA97/00018, incorporated herein by reference. Such media enhance water purification by removing unwanted ions by ion exchange. Further, such media facilitate migration of ions towards membranes **28** and **30** for subsequent permeation therethrough, as will be described hereinbelow.

Water to be treated is introduced into the diluting compartments **32** from supply stream **42**. Similarly, water or an aqueous solution is introduced into the concentrating compartments **18** and into the anode and cathode compartments **20, 22** from a supply stream **44**. A predetermined electrical voltage is applied between the two electrodes whereby anions in diluting compartments **32** permeate through anion exchange membranes **30** and into concentrating compartments **18** while cations in streams in diluting compartments **32** permeate through cation exchange membranes **28** and into concentrating compartments **18**. The above-described migration of anions and cations is further facilitated by the ion exchange material **40** present in diluting compartments **32**. In this respect, driven by the applied voltage, cations in diluting compartments **32** migrate through cation exchange resins using ion exchange mechanisms, and eventually pass through cation exchange membranes **28** which are in direct contact with the cation exchange resins. Similarly, anions in diluting compartments **32** migrate through anion exchange resins using ion exchange mechanisms, and eventually pass through anion

exchange membranes **30** which are in direct contact with the anion exchange resins. Aqueous solution or water introduced into concentrating compartments **18** from stream **44**, and anion and cation species which subsequently migrate into these compartments, are collected and removed as a concentrated solution from discharge stream **48**, while a purified water stream is discharged from diluting compartments **32** as discharge stream **50**.

By virtue of the current flowing between the cathode **26** in the cathode compartment **22** and the anode **24** in the anode compartment **20**, water is ionized into hydrogen and hydroxyl ions. Hydroxyl ions migrate through the anion exchange membrane **30** and become locally concentrated on the surface **52** of the concentrate compartment side of the anion exchange membrane **30**. This creates a localized region of high pH near this surface **52** of the anion exchange membrane **30**, thereby promoting the formation of scale.

Localized regions of high pH are also found at the cathode surface **54** of the electrodeionization unit. In this environment, reduction of water to form hydrogen gas, with the concomitant production of hydroxyl ion, is thermodynamically favourable. As a result, conditions near the cathode surface **54** also are conducive to the formation of scale.

To prevent the formation of scale on the surfaces **52** of the anion exchange membrane **30** and at the cathode surface **54**, an antiscalant supply **16** is provided for injecting antiscalant into the concentrate stream in loop circuit **12** for feed to concentrate compartment **18** and to anode compartment **20** and to cathode compartment **22**. Antiscalants may include sulphuric and hydrochloric acids to lower the pH; polyacrylic

acids, derivatives of polyacrylic acids (eg. co-polymers with sulfonate functional groups), phosphonate-type antiscalants, sodium hexametaphosphate; complexing agents such as EDTA, CDTA, amido succinic acid and the like chelating agents; and biocidal agents, preferably non-oxidizing, such as sodium bisulphite, and combinations thereof. In this respect, antiscalant supply **16** infuses an effective amount of antiscalant into concentrate compartment supply stream **44** and cathode electrolyte supply stream **38** to provide a concentration in the streams in the range of 1 to 500 parts per million (ppm). A desirable pH range for the concentrate stream to inhibit scaling in the electrodeionization units is about 2 to about 5, provided by about 500 to about 0.5 ppm for sulphuric acid and by about 365 to about 0.37 ppm for hydrochloric acid. A preferred concentration range for sodium hexametaphosphate is about 5 to about 200 ppm, most preferably in the range of 25 to 100 ppm. As a result, antiscalant circulates through both concentrate compartments **18** and cathode compartment **22,** inhibiting formation of scale, and is thereafter discharged through streams **48** and **60**, respectively, the concentrate stream being recycled with bleed stream **61** fed to a reverse osmosis unit, to be described, or passed to waste.

To recover and recycle antiscalant from the concentrate compartments **18,** discharge stream **48** is recirculated through line **12** with make-up solution containing antiscalant from injection unit **17** through feed line **16** for continuous supply of antiscalant to concentrate compartments **18** and to anode compartment **20** and to cathode compartment **22**. Antiscalant thus is used more efficiently in the process of the present invention by recovery and recycle of most of the unused antiscalant from the discharge of the electrodeionization unit **10**.

In the embodiment of the present invention illustrated in Figure **3**, electrodeionization unit **10** is operated in series with reverse osmosis unit **62** for the purification of water. Water to be treated is supplied into the reverse osmosis unit **62** by supply stream **64**, wherein the supplied water is separated into permeate stream **66** and retentate stream **68** by membrane **70**, well known in the art, and discharged to drain **72**. The permeate stream **66** is connected to supply stream **42** for further treatment in the electrodeionization unit **10**, whereas retentate stream **68** either is discharged to drain **72** or is used for other purposes, such as in cooling towers.

Scale deposition is also a phenomenon which adversely effects operation of the reverse osmosis unit **62**. In reverse osmosis, salt for example is separated from an aqueous salt solution by forcing water to flow through a membrane into a purified water phase by applying a pressure greater than the normal osmotic pressure, thereby overcoming the natural tendency of water to flow in the opposite direction. As a result, the saline solution becomes progressively more concentrated. In this extreme, the solubility limit of the dissolved salts are exceeded, leading to precipitation of $CaCO_3$ and other solids as scale. This mechanism of scale formation is fundamentally different from that in electrodeionization wherein the anion membranes' surfaces (concentrate side) are actively maintained at a high pH due to the migration of hydroxyl ions from water splitting in the diluting chambers; this high pH producing scaling.

Advantageously, a portion of antiscalant in circulating discharge stream **12** from the concentrate compartments **18** can be utilized in the reverse osmosis unit **62** by way of line **65** connected to supply water stream **64**. Loss of antiscalant from the electrodeionization unit **10** accordingly is reduced while scale formation in the reverse

osmosis unit **62** is inhibited.

In a further embodiment, antiscalant from concentrate compartment discharge in line **65** may be topped up before injection into reverse osmosis unit **36**. Referring to Figure **3**, a second antiscalant injection unit **67** may be provided upstream of the inlet of reverse osmosis unit **36** for addition of an effective amount of antiscalant to supplement the antiscalant from concentrate compartment discharge stream **34**, or to add a complementary agent.

Further variations to the embodiments illustrated in Figure **3** are contemplated and not limited to those shown. For example, permeate stream **66** may be further purified by passage through an additional reverse osmosis unit, to be described, or could be subjected to other separation processes, such as degasification, or other chemical treatments, or combinations thereof, prior to feed to the electrodeionization unit **10**.

To increase electrical conductivity in the electrodeionization unit **10** and, thereby, increase current flow with reduced voltage to reduce power consumption, another embodiment of the present invention provides for diverting a portion of permeate stream **66** of the reverse osmosis unit **62** to the electrodeionization unit **10** such that part of the permeate stream **69** is fed to the concentrate compartments **18**. Permeate stream **66** and retentate discharge stream **68** contain electrolytes, such as dissolved salt ions. Connection to either of these streams **66** or **68** could provide make-up of electrolyte and water in the concentrate compartment supply stream **44**. Preferably, retentate discharge stream **68** is not connected in this manner unless such retentate discharge stream **68** is relatively free of polyvalent cations, high molecular weight organic compounds and bacteria, which could otherwise foul the electrodeionization unit **10**. Therefore, if the

water supply stream **64** contains such impurities, line **69** from the permeate stream **66**, but not from the retentate stream **68**, may be connected to supply stream **44** for electrolyte make-up in the concentrate compartments **18** of the electrodeionization unit.

In a further embodiment of the present invention illustrated in Figure **4**, the water purification system of the invention consists of a multi-stage reverse osmosis system **70** in series with an electrodeionization unit **10**. The multi-stage reverse osmosis system **70** comprises two stages consisting of first and second reverse osmosis stages **72** and **74** respectively. Water to be purified is supplied to the first reverse osmosis unit **70** by supply stream **76**, together with a portion of the concentrate loop solution in line **12** by way of line **77** and is separated into a first permeate stream **78** and first retentate stream **80** by membrane processes occurring therein. Retentate stream **80** is discharged into the second reverse osmosis unit **74** and is subjected to membrane processes therein, causing separation of first retentate stream **80** into second permeate stream **82** and second retentate stream **84**. The second permeate stream **82** joins the first permeate stream **78** and is connected to supply stream **42** to the electrodeionization unit **10** for further treatment. The second retentate stream **84** either is discharged to drain **88**, or used for other purposes such as in cooling towers. To provide electrolyte make-up in the feed to the concentrate compartment **18** of the electrodeionization unit **10**, a bleed from second permeate stream **82** by line **83**, or from supply stream **42** for a combination of permeate streams **78, 82** through line **85** can be added to recycle stream **44** to the concentrate compartments **18**.

Antiscalant from the concentrate compartment discharge in line **77** can be topped up by a second antiscalant injection unit **79**.

It will be understood that the number of reverse osmosis stages in the reverse osmosis system is not limited to two, and could include any plurality of stages, hereinafter denoted as "n-stages", each containing a reverse osmosis unit, so as to effect economic purification and recovery of water. In this respect, the retentate streams from stages 1 through (n-1) are successively discharged into the following downstream reverse osmosis stages **2** through n for further treatment. The retentate stream from stage n is discharged to drain or used for other purposes requiring water of a lesser purity. Each of the permeate streams from the n-stages would combine into one header connecting to supply stream **42** for further purification in the electrodeionization unit **10**. A bleed may be taken from any of these permeate streams for connection to supply stream **44** of the concentrate compartments for increasing electrical conductivity in the electrodeionization unit **10**.

A further embodiment of the present invention is illustrated in Figure **5**, wherein a reverse osmosis system **88** comprises a multiple-pass serial reverse osmosis system consisting of a plurality of reverse osmosis units in series, the number of passes corresponding to the number of such reverse osmosis units, each reverse osmosis unit effecting further purification of the permeate stream from the reverse osmosis unit preceding it. In the example of such embodiment particularly depicted in Figure **5**, the number of such passes is two, consisting of the two reverse osmosis units **90** and **100** in series. In this embodiment, water to be purified together with antiscalant from a portion of the concentrate loop solution in line **12** by way of line **103** is provided in supply stream **92** to reverse osmosis unit **90**, and is separated into a first permeate stream **94** and first retentate stream **96** by membrane processes occurring therein. The first permeate

stream **94** is discharged into the second reverse osmosis unit **100** for further purification, while retentate stream **96** is discharged to drain. In the second reverse osmosis unit **100**, the first permeate stream **94** is separated into second permeate stream **102** and retentate stream **104** by membrane processes occurring therein. The second permeate stream **102** is connected to the electrodeionization unit **10** as supply stream **42** for further purification. Retentate stream **104** is either recycled back to supply stream **92**, discharged to drain or can be used as electrolyte. Supplemental antiscalant can be provided by a second antiscalant injection unit **93**

To provide electrolyte make-up to the concentrate compartments **18** of the electrodeionization unit **10**, a bleed **95** from either of first permeate stream **94**, or a bleed **99** from second permeate stream **102**, may be connected to supply stream **44** for the concentrate compartments **18**. Retentate stream **104** from the second reverse osmosis unit **100** may also be used through line **105** for electrolyte make-up because stream **104** has already been subjected to purification in the first reverse osmosis unit **90**, and is therefore relatively free of undesirable particles, organics and bacteria. Further, it is usually preferable to bleed from second retentate stream **104** wherein saline concentration is highest and, therefore, more likely to increase conductivity in electrodeionization unit **10**.

It will be understood that the number of reverse osmosis passes in the reverse osmosis system **88** is not limited to two, and could include any plurality of passes, each containing a reverse osmosis unit and each having one or more stages. In this respect, the permeate streams from the passes are each discharged into a corresponding downstream reverse osmosis unit for further treatment. The permeate stream from the

last pass is discharged into the electrodeionization unit **10** for further purification. Each of the retentate streams from the passes, with the exception of the first pass, is either recycled back to the inlet stream of the reverse osmosis unit of the first pass or is discharged to drain. A bleed may be taken from any of the permeate streams, or from any of the retentate streams with the exception of the retentate stream from the reverse osmosis unit of the first pass, for connection to supply stream **44** of the concentrate compartments **18** for increasing conductivity in the electrodeionization unit **10**.

In a further embodiment of the invention, shown in Figure **6**, the retentate streams from each of the passes may be discharged into a second stage reverse osmosis unit for further purification, yielding a further permeate stream to join a corresponding permeate stream from the same pass for further purification in a downstream reverse osmosis pass or in the electrodeionization unit **10**. This variant combines aspects of each of the processes illustrated in Figures **4** and **5** and comprises two passes consisting of two stages each, each stage having one reverse osmosis unit. Therefore, the first pass comprises of first reverse osmosis stage **110** and second reverse osmosis stage **120**, and the second pass comprises of third reverse osmosis stage **130** and fourth reverse osmosis stage **140**. Water to be purified together with a portion of the concentrate loop recycle solution in line **12** by way of line **115** and supplemental antiscalant injection unit **113** is supplied to the first reverse osmosis unit **110** by supply stream **112**, and is separated into first permeate stream **114** and first retentate stream **116** by membrane processes occurring therein. Retentate stream **116** is discharged into the second reverse osmosis stage **120**, and subjected to membrane processes therein, causing separation of first retentate stream **116** into second permeate stream **122** and second retentate stream **124**. The second

permeate stream **122** joins the first permeate stream **114** to become supply stream **132** to the second pass for further treatment in the third reverse osmosis unit **130**. The second retentate stream **124** is discharged to drain. Supply stream **132** enters the third reverse osmosis unit **130** and is separated into third permeate stream **134** and third retentate stream **136** by membrane processes occurring therein. Retentate stream **136** is discharged into the fourth reverse osmosis stage **140**, and subjected to membrane processes therein, causing separation of third retentate stream **136** into fourth permeate stream **142** and fourth retentate stream **144**. The fourth permeate stream **142** joins the third permeate stream **134** to connect to supply stream **42** for further purification in the electrodeionization unit **10**. The fourth retentate stream **144** either is connected back to feed stream **112** to the first reverse osmosis unit **110** by line **145** or discharged to drain.

To effect electrolyte make-up in the concentrate compartments **18** of the electrodeionization unit **10**, a bleed from either of first permeate stream **114**, second permeate stream **122**, third permeate stream **134**, fourth permeate stream **142** or fourth retentate stream **144**, or combinations thereof, may be connected to supply stream **44** by line **123** for feed to the concentrate compartments **18**. It is most preferable to bleed from second permeate stream **122** through line **123** where saline concentration is highest and, therefore, more likely to increase conductivity in electrodeionization unit **10**.

It is understood that the number of reverse osmosis passes and the number of reverse osmosis stages therein are each not limited to two, and could include any plurality of passes, so as to cause economic purification and recovery of water. Bleeds from any permeate or retentate stream from associated reverse osmosis units, with the exception of the retentate streams in the first pass, may be connected to the electrodeionization unit

10 for increasing conductivity thereof.

Further variations to the embodiments illustrated in Figures **4**, **5** and **6** are contemplated and not limited to those shown in the Figures. For example, prior to connection to the supply stream **42** to the diluting compartments **32** of the electrodeionization unit **10**, permeate streams from the reverse osmosis unit(s) may be subjected to further purification by separation processes, such as degasification. Additionally, unused antiscalant from the circulating loop **12** of the concentrate compartments **18** in the electrodeionization unit **10** preferably are connected to the supply streams for the reverse osmosis unit for inhibiting the formation of scale in that reverse osmosis unit, and any other downstream units, in a similar manner as the embodiment depicted in Figure 3.

The present invention provides a number of important advantages. The antiscaling agents including pH control agents, antifouling scale suppressing agents, chelating agents and the like can be used in the electrodeionization unit in higher than normally commercially viable concentrations because of containment of the agents within the system by recycle within the electrodeionization unit and by recycle to one or more reverse osmosis units in series. This recycling of a relatively small flow of fluid from the electrodeionization unit into the larger influent flow to the reverse osmosis unit results in a suitably low concentration of antiscalant for economical reverse osmosis operation. The selective use of reverse osmosis permeate as make-up to the recycle loop to the concentration compartments utilizes salinity of the permeate to enhance electrical conductivity and efficiency of the cells with increased current flow at reduced voltages, thereby reducing electrical power requirements without the need and cost of separately

adding salt to the system.

It will be understood, of course, that modifications can be made in the embodiments of the invention described herein without departing from the scope and purview of the invention as defined by the appended claims.

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We claim:

1. A method for inhibiting formation of scale in an electrodeionization unit for deionizing water having an anode compartment at one end of the unit, a cathode compartment at the opposite end of the unit, and a plurality of diluting compartments alternating with concentrating compartments positioned between the said anode and cathode compartments, comprising:

passing feed water to be deionized through the diluting compartments;

passing water or an aqueous solution for accepting ions from the feed water through the concentrating compartments, and through the anode and cathode compartments;

applying an electrical voltage between the said anode and the said cathode whereby ions in the feed water migrate to the water or aqueous solution in the concentrating compartments;

collecting and discharging aqueous solution from the anode and cathode compartments;

recycling water or aqueous solution from the concentrating compartments as a concentrate stream through the concentrating compartments and through the anode and cathode compartments; and

injecting an antiscalant to the concentrate stream recycling through the concentrating compartments and through the anode and cathode compartments in an amount effective to inhibit scale formation in the concentrating compartments and in the cathode compartment.

2. A method as claimed in claim 1 in which the effective amount of antiscalant in

the concentrate stream is in the range of 1 to 400 ppm.

3. A method as claimed in claim 2 in which the antiscalant is selected from the group consisting of sulphuric acid, hydrochloric acid, polyacrylic acid, derivatives of polyacrylic acids co-polymered with sulfonates, phosphonate-type antiscalants and sodium hexametaphosphate, EDTA and CDTA complexing agents, amido succinic acid chelating agent, non-oxidizing biocidal agents typified by sodium bisulphite, and combinations thereof.

4. A method for purifying and deionizing water for inhibiting formation of scale in a reverse osmosis unit comprising one or more stages and in an electrodeionization unit in series in which water to be purified and deionized passes through the reverse osmosis unit to produce a permeate stream and a retentate discharge stream, and in which the electrodeionization unit has an anode compartment at one end of the unit, a cathode compartment at the opposite end of the unit, and a plurality of diluting compartments alternating with concentrating compartments positioned between the said anode and cathode compartments, comprising:

passing feed water to be purified and deionized through the reverse osmosis unit;

passing permeate from the reverse osmosis unit through the diluting compartments of the deionization unit;

passing water or an aqueous solution for accepting ions from the feed water through the concentrating compartments, and through the anode and cathode compartments;

applying an electrical voltage between the said anode and the said cathode whereby ions in the feed water migrate to the water or aqueous solution in the

concentrating compartments;

collecting and discharging aqueous solution from the anode and cathode compartments;

recycling water or aqueous solution from the concentrating compartments as a concentrate stream through the concentrating compartments and through the anode and cathode compartments;

injecting an antiscalant to the concentrate stream recycling through the concentrating compartments and through the anode and cathode compartments effective to inhibit scale formation in the concentrating compartments and in the cathode compartment;

bleeding a portion of the concentrate stream containing antiscalant;

combining and passing said portion of the bled concentrate containing an amount of antiscalant with the feed water through the reverse osmosis unit, adjusting the amount of antiscalant in the water to the reverse osmosis unit to provide an effective amount of antiscalant to inhibit scale formation in the reverse osmosis unit, and passing the permeate stream through the dilute compartments of the deionization unit.

5. A method as claimed in claim 4, adjusting the antiscalant in the water to the reverse osmosis unit to an amount in the range of 1 to 75 ppm effective to inhibit scaling.

6. A method as claimed in claim 5 in which at least a portion of the permeate of one or more stages is added to the concentrate stream passing through the concentrating compartments and through the anode and cathode compartments to add electrolyte thereto, thereby increasing electrical conductivity.

7. A method as claimed in claim 4, subjecting said feed water to the reverse osmosis units to a plurality of passes, each pass comprising one or more stages, wherein permeate from at least one of the stages or one of the passes is combined with the concentrate stream for passage through the concentrating compartments and through the anode and cathode compartments to add electrolyte thereto, thereby increasing electrical conductivity.

8. A method as claimed in claim 7 in which retentate from at least one of the stages, excepting from the first reverse osmosis pass, is combined with the concentrate stream for passage through the concentrating compartments and through the anode and cathode compartments to add electrolyte thereto, thereby increasing electrical conductivity.

9. A method as claimed in claim 5 in which the antiscalant is selected from the group consisting of sulphuric acid, hydrochloric acid, polyacrylic acid, derivatives of polyacrylic acids co-polymerized with sulfonates, phosphonate-type antiscalants, sodium hexametaphosphate, EDTA and CDTA complexing agents, amido succinic acid chelating agent, non-oxidizing biocidal agents typified by sodium bisulphite, and combinations thereof.

10. A method as claimed in claim 1, in which the antiscalant is sulphuric acid in the range of about 500 to 0.5 ppm or hydrochloric acid in the range of about 365 to about 0.4 ppm.

11. A method as claimed in claim 1, in which the antiscalant is sodium hexametaphosphate in an amount in the range of about 5 to about 200 ppm.

12. A method as claimed in claim 1, in which the antiscalant is sodium hexametaphosphate in an amount in the range of about 25 to about 100 ppm.

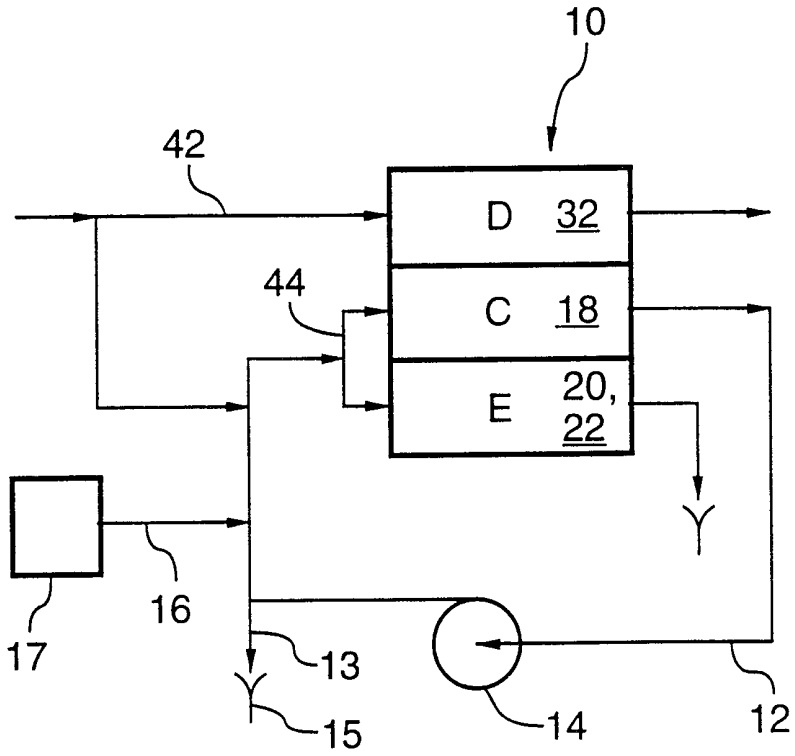


FIG.1

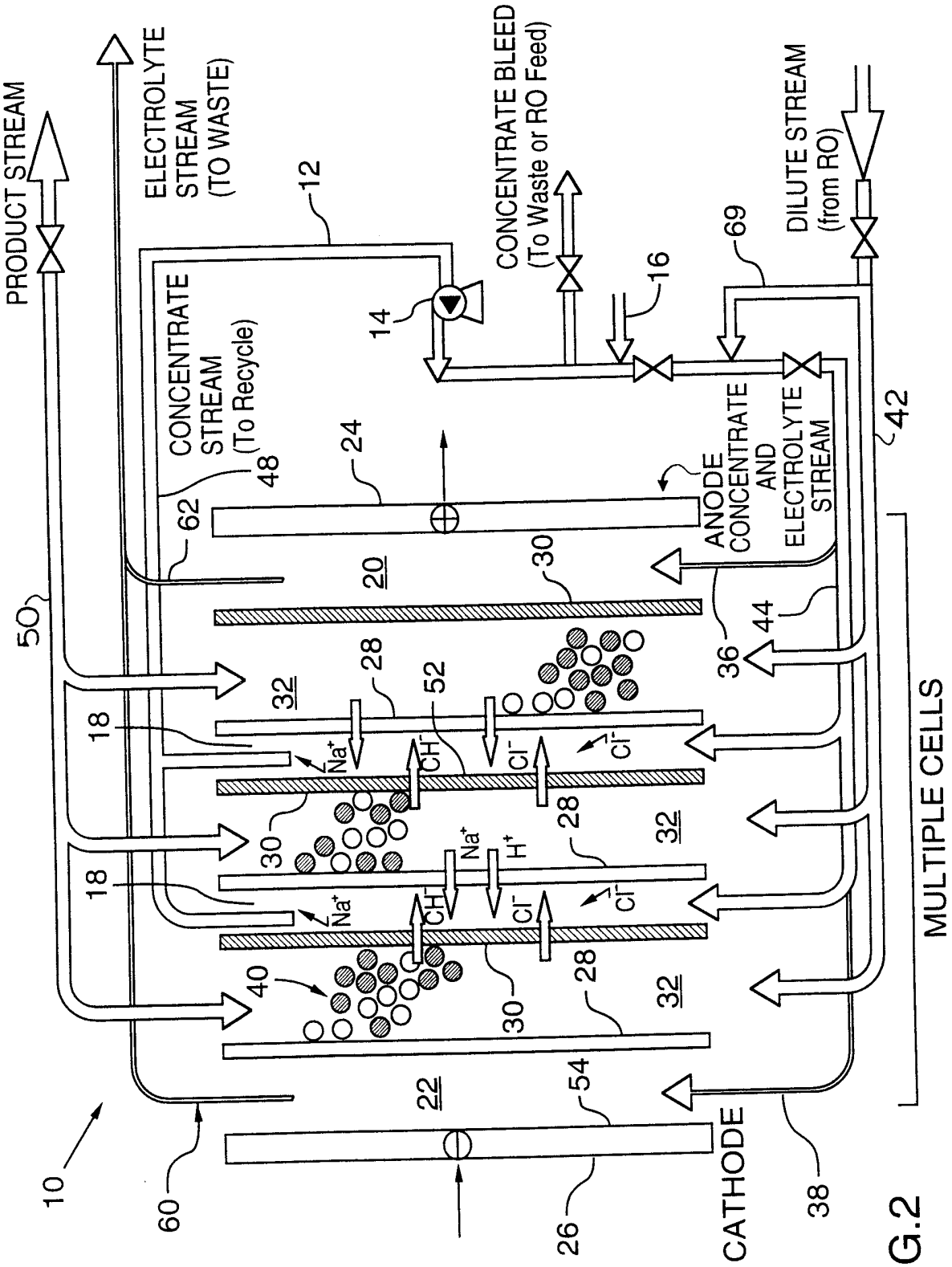

PRODUCT STREAM
ELECTROLYTE STREAM (TO WASTE)
CONCENTRATE BLEED (To Waste or RO Feed)
DILUTE STREAM (from RO)
CONCENTRATE STREAM (To Recycle)
ANODE CONCENTRATE AND ELECTROLYTE STREAM
MULTIPLE CELLS
CATHODE
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Na+
H+
Cl-
CH-

FIG.2

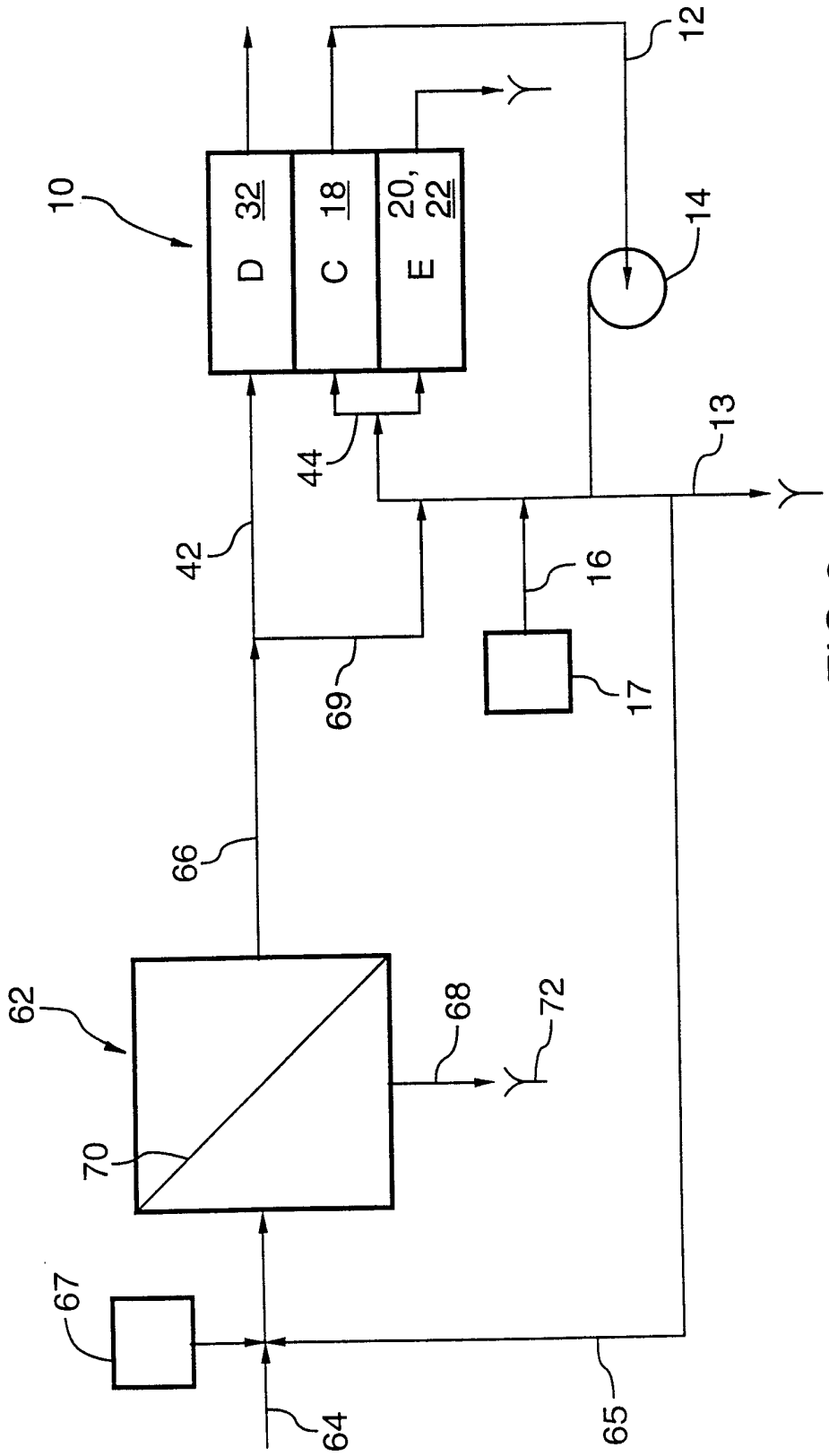


FIG.3

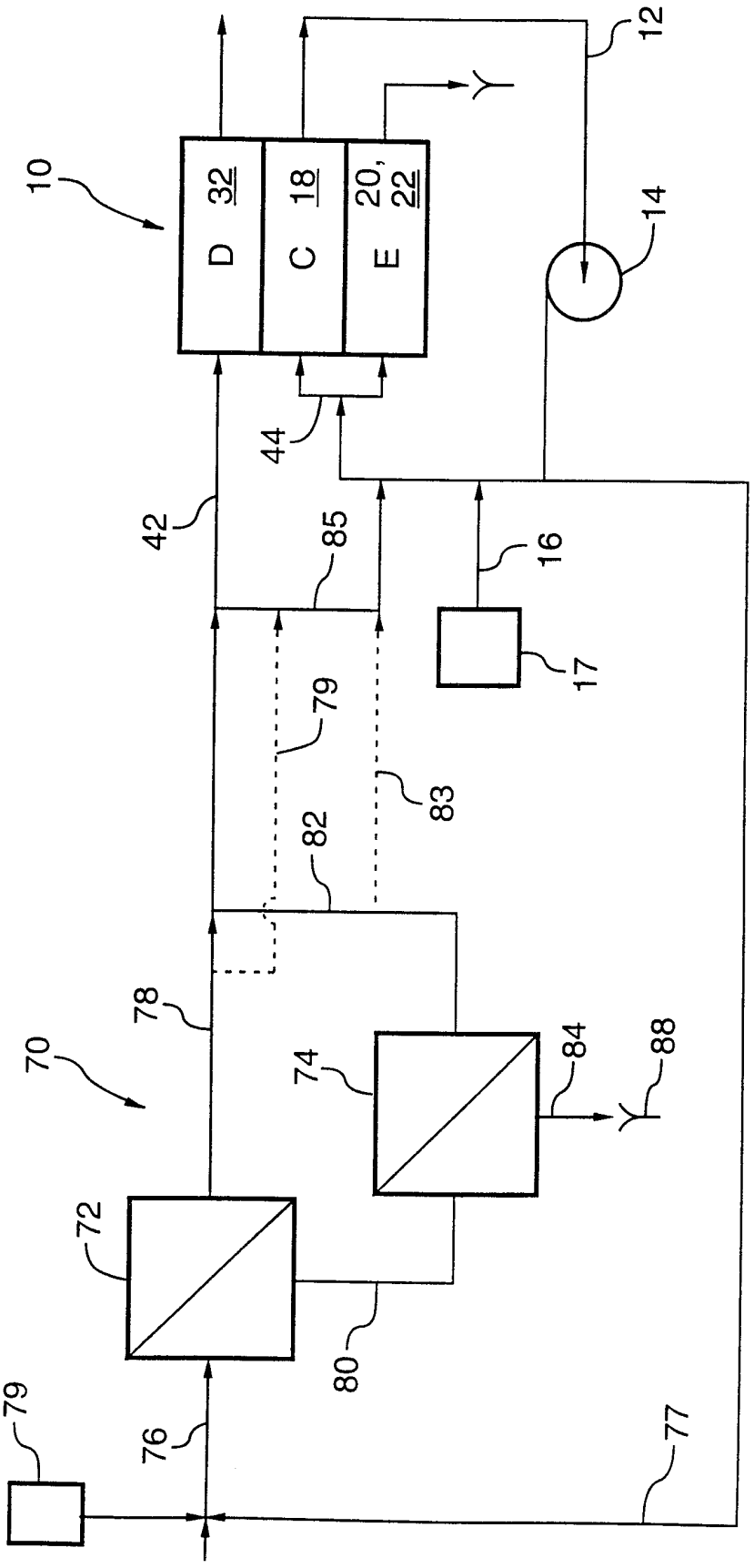

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FIG.4

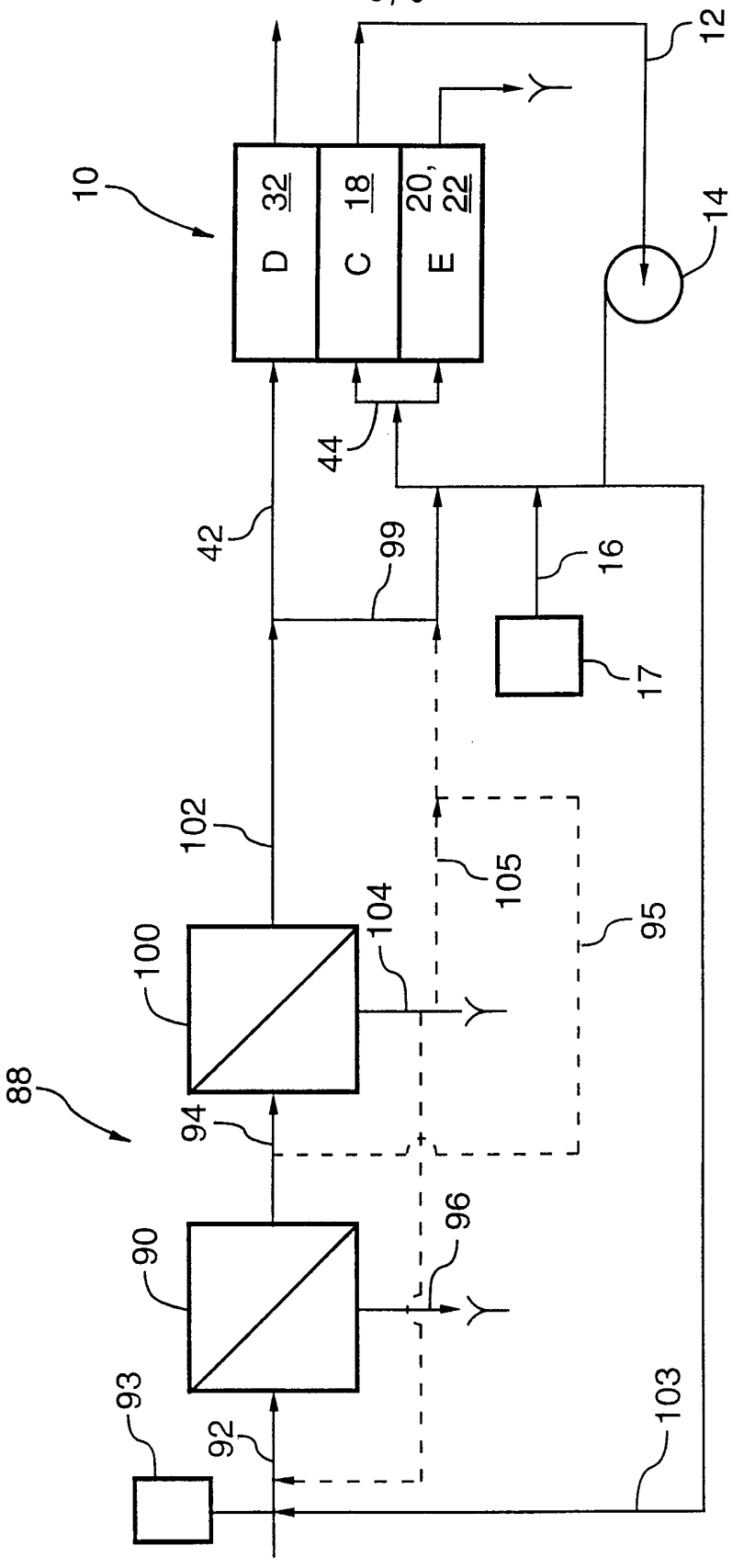

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FIG.5

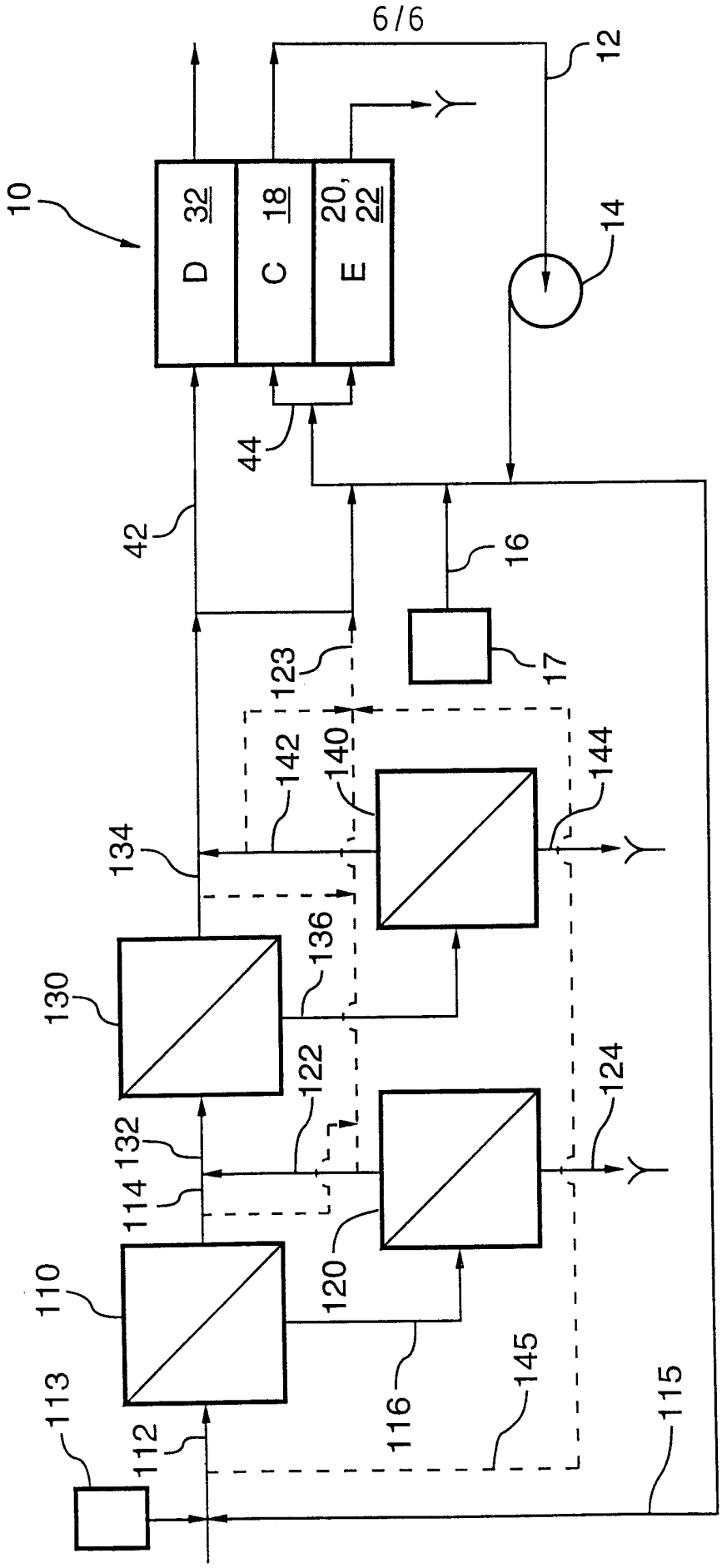

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FIG.6

INTERNATIONAL SEARCH REPORT

Inte ɔnal Application No
PCT/CA 99/00594

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 B01D61/52 B01D61/48 B01D61/58 C02F1/469

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)
IPC 7 B01D C02F

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 practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 012, no. 011 (C-468), 13 January 1988 (1988-01-13) -& JP 62 168508 A (FUJITSU GENERAL LTD), 24 July 1987 (1987-07-24) abstract -& DATABASE WPI Section Ch, Derwent Publications Ltd., London, GB; Class D15, AN 1987-246455 XP002118256 abstract -& CHEMICAL ABSTRACTS, vol. 107, no. 22, 30 November 1987 (1987-11-30) Columbus, Ohio, US; abstract no. 204870, XP002118253 abstract	1-3,10
A	-/--	4

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
8 October 1999	22/10/1999

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Hoornaert, P

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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.

X	EP 0 839 762 A (EBARA CORP) 6 May 1998 (1998-05-06) abstract; claims 1-4; figure 1 column 1, line 1 - line 45 column 3, line 56 -column 4, line 4 column 4, line 13 - line 22 column 4, line 47 -column 5, line 34	1-3

X	US 3 003 940 A (MASON) 10 October 1961 (1961-10-10) column 1, line 12 - line 26 column 2, line 6 - line 58 column 4, line 12 - line 46 column 5, line 73 -column 6, line 34 claims 1-3,7,8; figure 3; examples 1-3	1-3,10

X	PATENT ABSTRACTS OF JAPAN vol. 007, no. 014 (C-146), 20 January 1983 (1983-01-20) -& JP 57 171485 A (KOBE SEIKOSHO KK), 22 October 1982 (1982-10-22) abstract -& DATABASE WPI Section Ch, Derwent Publications Ltd., London, GB; Class D15, AN 1982-03236J XP002118257 abstract -& CHEMICAL ABSTRACTS, vol. 98, no. 8, 21 February 1983 (1983-02-21) Columbus, Ohio, US; abstract no. 59705, XP002118254 abstract	1-3,11, 12
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INTERNATIONAL SEARCH REPORT

Inter nal Application No
PCT/CA 99/00594

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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INTERNATIONAL SEARCH REPORT

formation on patent family members

Inter nal Application No
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