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ELECTRODIALYSIS

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Fig. 1

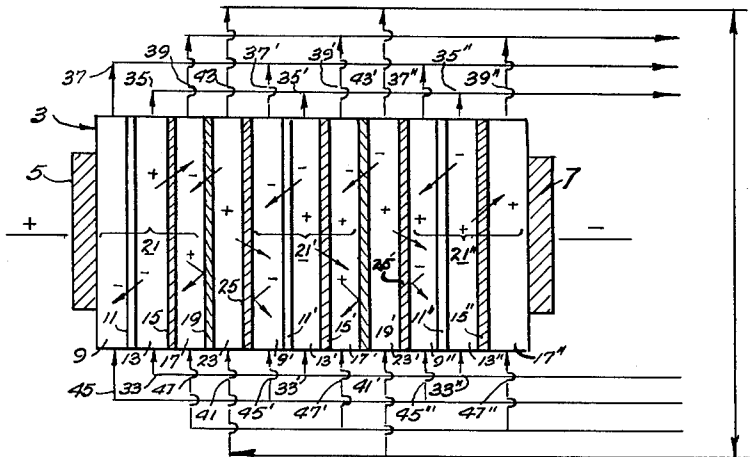
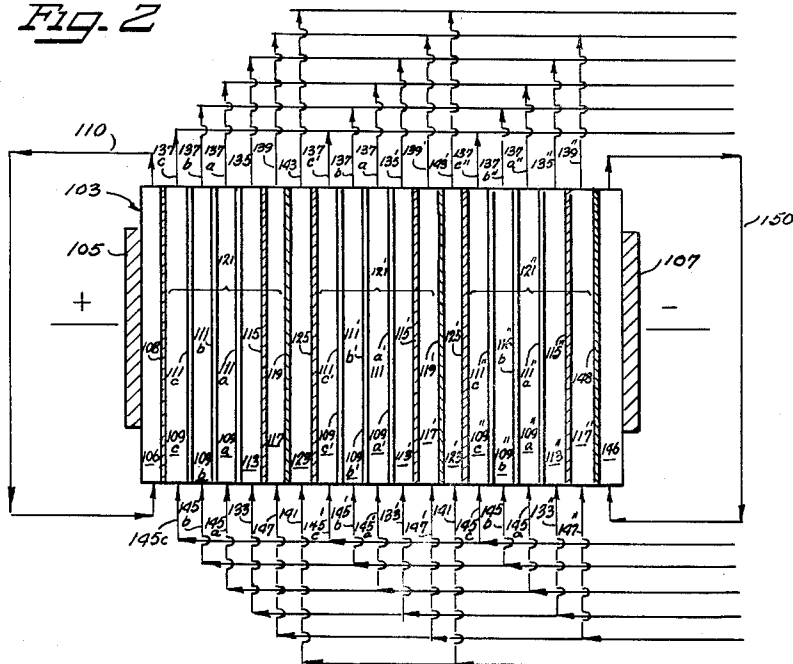


Fig. 2



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ELECTRODIALYSIS

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The present invention relates generally to electrodi-
alysis, and more particularly, it relates to more efficient
means for electro dialyzing aqueous solutions.

Electrodialysis is a known electro-chemical processing
means for treating solutions by the application, in a cell,
of an electrical potential between two electrodes which
are usually referred to as the anode, which is positively
charged, and the cathode, which is negatively charged.
Between these electrodes is disposed one or more mem-
branes to divide the cell into a series of adjacent com-
partments, which are referred to herein as frames. Upon
the application of an electrical potential between the
anode and cathode, an influent liquid is electro dialyzed,
whereby certain constituents of the liquor migrate toward
the anode and other constituents toward the cathode,
whereby fractional separation of the constituents occurs.
The solution in the frame adjacent the anode is gen-
erally referred to as the anolyte and the solution in the
compartment adjacent the cathode is generally referred
to as the catholyte. The frame formed between the two
membranes may contain the liquor.

It will be seen that upon the application of electrical
potential between the anode and cathode, two solutions
can be obtained from the liquid and a remaining or
residual solution can be obtained from the liquor. The
above arrangement in a cell has been known hereto-
fore. However, it has not been possible, heretofore, to
arrange the frames so that more than one such series
of frames can be set up between the anode and cathode
to treat solutions containing large molecular weight com-
pounds such as ligno-sulfonic ions and amino ions. In
other words, when it is desired to recover two solutions
from a solution containing large molecular weight ions,
it has not been economically feasible to treat the solu-
tion in commercial operations.

A principal difficulty with utilizing only three frames,
i.e., an anolyte frame, a catholyte frame and a liquor
frame, which together are referred to herein as a "treat-
ing frame," is the inefficiency of the operation of the
system. In this connection, most of the resistance in
an electro dialysis cell having a single treating frame
occurs in the region of the electrode, i.e., the anode or
the cathode. Accordingly, to have an efficient operation
it is necessary that there be many frames between the
electrodes to provide efficiency of operation.

The stacking of frames between electrodes is known
in connection with the removal of one solution from an
influent. A particular example of this occurs in the
electrodialysis of sea water to provide potable water from
the sea water. With such arrangement, the efficiency
of the unit is greatly increased so that it becomes an
economic operation. However, such arrangements, hereto-
fore, have been primarily used when there is to be
recovered a single solution or fractions of such single
solution.

It has not been known, heretofore, how to stack treat-
ing frames so as to efficiently treat liquors or solutions
containing high molecular weight ions in such manner
as to recover the high molecular weight ions from the
liquor. Accordingly, it has not been known how to
treat such solutions as spent sulphite liquor in a prac-
tical manner. In this connection, spent sulphite liquor
results from the digestion of wood in a cooking liquor

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in the paper making process and it includes sulfonate
compounds which are generally ligno-sulfonates of vary-
ing molecular weight, wood sugars, sulfur dioxide and
basic ions, such as sodium, calcium, magnesium and
ammonium ions, depending upon the nature of the diges-
tion treatment. As indicated, the ligno-sulfonates are
generally high in molecular weight but the lower molecu-
lar weight ligno-sulfonates and sugars are desirably sepa-
rated from the higher molecular weight ligno-sulfonates
and sugars to provide desired fractions. It is, of course,
desirable to separate out the basic and acid ions so that
they can be re-utilized in the preparation of additional
cooking liquor for the paper making process.

Accordingly, it is desirable to take the spent sulphite
liquor and recover the basic ions in the catholyte and
recover ligno-sulfonates and sugars in the anolyte. As
before indicated, this system is desirable, but, hereto-
fore, has been uneconomic because of the lack of a
satisfactory cell for effecting the desired treatment.

Other solutions or dispersions which can be desirably
treated are salt-protein systems, such as milk, blood, whey,
etc. In such systems anions and cations can be sepa-
rated out and protein compounds recovered.

A principal object of this invention is, therefore, the
provision of an efficient electro dialysis cell which will
provide from an influent or liquor containing high molecu-
lar weight ions an anion concentrating solution or cation
concentrating solution containing such ions. A more par-
ticular object of this invention is to provide improved
apparatus for treating spent sulphite liquor and for treat-
ing other liquors from which it is desired to recover,
efficiently, two or more solutions, one of which solu-
tions contain high molecular weight ions. Other objects
and advantages of this invention will become apparent
by reference to the following description and accompany-
ing drawing in which:

FIGURE 1 is a schematic drawing of an electrodi-
alysis cell of the invention in which three treating frames
are disposed between an anode and a cathode, from
which cell three solutions are recovered, one solution
being an anion concentrating solution containing high
molecular weight compounds, another solution being a
cation concentrating solution, and a third solution being
a treated liquor of suitable concentration; and

FIGURE 2 is a modified cell of the invention compris-
ing three treating frames disposed between an anode and
a cathode, from which treating frames are recovered a
cation concentrating solution, a concentrated liquor, and
three separate concentrated anion fractions.

For purposes of this application and as previously indi-
cated, certain terms will be used in describing the inven-
tion and are defined herein. In this connection, a
"frame" is referred to as any compartment between two
membranes, or between a membrane and an electrode.
A "treating frame" is referred to herein as a series of
frames associated with the influent and includes the
frames containing the anion concentrating solution, the
liquor and the cation concentrating solution. A treat-
ing frame may also include frames containing fractions
of the anion concentrating and cation concentrating solu-
tions. The term "cell" includes the electrodes, the mem-
branes and all of the frames disposed between the elec-
trodes. The term "barrier frame," as will appear more
clearly hereinafter, is a frame disposed between treat-
ing frames.

The membranes utilized in the apparatus of the in-
vention include selective membranes and non-selective
membranes. A non-selective membrane will pass both
anions and cations, but may be sized to control the pas-
sage of certain sized molecules. The selective mem-
branes, which may also be sized to pass different sized

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molecules, are selective in the sense that they are charged so that anions can pass therethrough and cations are rejected, or vice versa. A cation selective membrane will pass cations and will not pass anions, whereas an anion selective membrane will pass anions and will not pass cations. These selective membranes and non-selective membranes are commercially available.

This invention, in its simplest form, comprises two treating frames disposed between an anode and a cathode, each treating frame including a liquor frame having a non-selective membrane on one side thereof. The treating frames are separated from one another by a barrier frame which contains an electrolyte for conducting current comprising anions and cations which are not deleterious to the anion and cation concentrating solutions.

Thus, the apparatus of this invention, in its simplest form, comprises a cell having a cathode, surrounding which is a cation concentrating frame in which basic ions are recovered. In the simplest form of the invention, the cation concentrating frame is also a catholyte frame. Adjacent the cation concentrating frame is a liquor frame which receives the influent to be treated, and which has a non-selective membrane on one side thereof. Next, adjacent the liquor frame, is an anion concentrating frame in which the acidic ions and some normally non-ionic compounds are recovered. These three frames comprise a first treating frame. Then, adjacent this anion concentrating frame is a barrier frame containing the electrolyte which is not deleterious to the anion or cation concentrating solutions. On the other side of the barrier frame is a second treating frame comprising a cation concentrating frame adjacent which is a liquor frame, also having a non-selective membrane on one side thereof, followed by an anion concentrating frame or anolyte frame in which is disposed the anode of the cell.

It will be apparent that by using barrier frames intermediate the treating frames, any number of treating frames can be stacked in accordance with this invention. This being the case, the efficiency of a cell can be greatly increased because the relative power loss caused by the resistance around two electrodes is reduced in proportion to the number of treating frames stacked between the electrodes.

Of course, there needs to be particular selection of membranes between the frames. In this connection, selective membranes are utilized on either side of the barrier frames. The utilization of selective membranes makes sure that the anions and cations of the barrier solution go into the cation and anion concentrating solutions respectively and there is no dilution of these concentrating solutions by ion transfer to the barrier solution. One of the membranes between the liquor frame and the anion or cation concentrating frames may be selective so that the ions will travel from the liquor frame into the anion or cation concentrating frames and not from these frames into the liquor frame. One of the membranes between the liquor frame and the anion or cation concentrating frames should be non-selective. This is done in order to get transfer of desired large molecular weight molecules into the anion or cation concentrating solution without burning of the membrane. As previously indicated, this use of non-selective membranes with the liquor frame to pass the large molecules is an important feature of this invention.

By suitable selection of the membranes, there can be effected separation of an anion or cation concentrating solution into various fractions. In this connection, several anion or cation concentrating frames may be adjacent one another and be separated by differing membranes, thereby obtaining different fractions of the anion or cation concentrating solution. This will become more apparent in connection with the description of FIGURE 2 in the drawings hereinafter.

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Now referring to FIGURE 1 of the drawings, the overall electro dialysis cell is designated by the numeral 3. In the cell 3, are a positive electrode referred to as the anode 5 and also in the cell is a negative electrode referred to as the cathode 7. Immediately adjacent to anode 5 is an anion concentrating frame 9. Thus, in this instance, the anion concentrating frame 9 is also an anolyte frame. The anion concentrating frame is bounded on one side by a non-selective membrane 11. On the other side of this non-selective membrane 11 is a liquor frame 13 which is bounded on the other side by a selective membrane 15. The selective membrane 15 also provides one boundary for a cation concentrating frame 17 which is bounded on the other side by a selective membrane 19. The anion concentrating frame 9, the liquor frame 13, and the cation concentrating frame 17 comprise together a treating frame designated generally by the numeral 21. This particular treating frame is designed for handling liquor which comprises anions having large molecular weight.

The treating frame 21 is disposed adjacent a barrier frame 23 which is disposed between the selective membrane 19 and another selective membrane 25. On the other side of the barrier frame 23 is another treating frame which comprises the same elements as the treating frame 21 and is designated by the numeral 21'. Since the treating frame 21' includes the same elements as the treating frame 21, corresponding parts are indicated by the same numerals and are differentiated from the elements of the treating frame 21 by the symbol prime (''). Adjacent the treating frame 21' is a barrier frame which is similar to the barrier frame 23 and is designated with the numeral 23'.

The apparatus illustrated in FIGURE 1 further includes a third treating frame which is designated by the numeral 21'' and the elements of this frame are the same as in the treating frames 21 and 21' and are designated by corresponding numerals to the liquor frames 21 and 21', but are differentiated therefrom by the designation double prime ('').

It will be readily apparent that the electrolytic cell can comprise as many treating frames as may be desired, which liquor frames are separated by barrier frames, as illustrated in FIGURE 1.

For purposes of describing the operation of the cell, the function of liquor frame 21 and barrier frame 23 will be described in detail, but it will be understood that similar operations occur in liquor frames 21' and 21''.

The liquor to be treated enters the liquor frame 13 through the line 33. The cations travel through the selective membrane 15 into the cation concentrating frame 17. The anions travel through the non-selective membrane 11 into the anion concentrating or anolyte frame 9. The treated liquor exits from the liquor frame through the line 35, the anion concentrating solution leaving the anion concentrating frame through the line 37 and the cation concentrating solution leaving the cation concentrating frame through the line 39.

The barrier solution enters the barrier frame through the line 41 and exits from the frame through the line 43.

The anion concentrating solution, the cation concentrating solution and the barrier solution may, under certain conditions and objectives, be re-circulated, the anion solution entering the anion concentrating frame through the line 45 and the cation solution entering the cation concentrating frame through the line 47.

As before indicated, the treating frames 21' and 21'' function in a similar manner, as has been described in connection with the liquor frame 21. Accordingly, the influent and effluent lines are similarly designated, but are differentiated by the symbols of prime ('') and double prime ('').

The barrier solution desirably comprises anions and cations which may be utilized in the desired operation.

Thus the barrier solution may comprise an acid such as sulphuric acid, sulphurous acid, or acetic acid with the anions travelling into the cation concentrating solution and the hydrogen ions going into the anion concentrating solution. In order to provide the desired efficiency of operation, it is quite apparent that the barrier solution should be a good electrolyte and readily able to pass the current between the anode and the cathode.

Now referring to FIGURE 2 in the drawings, this figure also discloses a cell which is generally designated by the numeral 103. This cell comprises an anode 105 and a cathode 107. The cell 103 comprises three treating frames 121, 121' and 121''.

The treating frame 121 includes a liquor frame 113 which is adjacent a series of anion concentrating frames 109a, 109b and 109c. The liquor frame 113 is separated from the anion concentrating frames 109a, 109b, and 109c by a series of non-selective graded membranes 111a, 111b, and 111c. Between the anode 105 and the first anion concentrating frame 109c is disposed an anolyte frame 106 which is separated from the anion concentrating frame 109c by a selective membrane 108.

The liquor frame 113 is separated from a cation concentrating frame 117 by a selective membrane 115. Thus, this treating frame is also primarily adapted to handle liquor having anions of high molecular weight.

The treating frame 121 is bounded by a barrier frame 123 through a membrane 119 which is a selective membrane.

The barrier frame has a membrane 125 on the other side.

The liquor is introduced into the liquor frame 113 through the line 133 and concentrated liquor leaves the liquor frame through the line 135.

The various anion concentrating solutions exit from the treating frame through the lines 137a, 137b and 137c. This cation concentrating solution enters the treating frame through the line 147, and exits through the line 139. The anion concentrating solution is re-circulated and enters the anion concentrating frames through lines 145a, 145b and 145c. The barrier solution enters the barrier frame through line 141 and leaves this frame through the line 143.

The treating frames 121' and 121'' include the elements of the treating frame 121 and corresponding parts of the respective treating frames 121' and 121'' are differentiated from the parts of the treating frame 121 by the symbols prime (') and double prime (') respectively. The barrier frame, between the treating frame 121' and 121'', is designated 123'.

A catholyte frame 146 is disposed adjacent the cathode and is separated from the cation concentrating frame 117'' by a selective membrane 148. The electrolyte for the anode electrolyte frame 106 is circulated through line 110 and the electrolyte for the cathode electrolyte frame 146 is circulated through the line 150.

It will be seen that the cell shown in FIGURE 2 provides five fractions of the liquor. In this connection, the illustrated cell provides a cation concentrating solution, a concentrated liquor solution, and three anion concentrating solutions containing different fractions of the anion solution.

The cation membranes, such as the membranes designated 15, 15' and 15'' in FIGURE 1 and the membranes 115, 115' and 115'' in FIGURE 2, should be of the cation selective type and, in this connection, particularly satisfactory membranes are sold under the trade name Ionics CR-61. The anion membranes, such as membranes 11, 11' and 11'', in FIGURE 1, and the membranes 111a, 111a' and 111a'' in FIGURE 2 could be non-selective membranes, as for example Cellophane 600PT or Nalfilm D-30. The membranes, such as the membranes 19 and 19' shown in FIGURE 1, and 119 and 119' in FIGURE 2, are of the anion selective type, such

as Ionics AR-111 membranes. The membranes 25 and 25' shown in FIGURE 1 and the membranes 125 and 125' should be cation selective.

The membranes shown in FIGURE 2 between the various anion concentrating frames 109a, 109b and 109c, they being membranes 111a, 111b and 111c, are graded non-selective membranes having varying pore size to provide different fractions of the anion solution. The pore size is adjusted to pass molecules of the desired size so that fractionation may occur. By way of example, the membrane 111a may be selected to pass molecules having molecular weight of less than 5000, whereas the membrane 111b may be selected to pass molecules having molecular weights under 1000, and membrane 111c may be selected to pass low molecular weight ions, such as those having molecular weights below 200.

The choice and selection of the particular membranes is within the skill of the electrodialysis art and does not comprise a part of this invention. The fractionation of the anion concentrating solution in several adjacent frames with membranes of different pore sizes is also within the skill of the art.

In a particular example of this invention and referring to FIGURE 1 of the drawing, an ammonia base, spent sulphite liquor having a solids content of about 10% was used. The spent liquor had a nitrogen content of about 4 grams per liter and included lignin material having molecular weights between about 300 and about 300,000. The cation concentrating solution was introduced into the cation concentrating frames 17, 17' and 17'' and contained ammonia at a level of about 6 grams per liter based on nitrogen. The barrier frames 23 and 23' contained sulphurous acid in a concentration of about 6 grams per liter. The anion concentrating solution was sulphurous acid having a normality of 0.1. These solutions were circulated through the respective frames at a rate sufficient to establish turbulence. In operation of the cell, liquor was passed through the liquor frames 13 times and the aggregate residence time in the liquor frame was one minute.

An electrical potential was established between the anode 5 and the cathode 7 sufficient to establish a current density in the cell 3 of 30 milliamperes per square centimeter of membrane area.

The impressed voltage caused the ammonia ions in the liquor to pass from the liquor frames 13, 13' and 13'' through the cation selective membranes 15, 15' and 15'' into the cation concentrating frames 17, 17' and 17''. At the same time, sulphite ions from the barrier frames 23 and 23' passed into the cation concentrating frames 17 and 17' causing the formation of ammonium sulfite and bisulfite.

The membranes 11, 11' and 11'' were anion selective, and because of this only very low molecular weight compounds, particularly sugars, very low molecular weight ligno-sulfonates and sulfur dioxide, passed through the selective membranes 11, 11' and 11'' into the anion concentrating frames 9, 9' and 9''. At the same time, about 20 percent of the water in the liquor passed by osmosis into the anion concentrating frames 9, 9' and 9''. The higher molecular weight compounds remained in the liquor which exited from the cell 3 through lines 35, 35' and 35''.

With the use of anion selective membranes as described above, the resistance of the cell increased as the selective membranes became plugged with higher molecular weight anionic compounds until the unit became inoperative due to polarization with consequent overheating and burning of the membranes. When, however, non-selective membranes were used in positions 11, 11' and 11'', such plugging and destruction of the membranes did not occur.

The foregoing example described specific flow characteristics when operating with the substrates and dilutions indicated. Extensive operation has demonstrated that

various concentration and dilution effects are obtained as the osmotic and electrodialytic conditions are altered to meet specific requirements. Such variations are deemed to be within the scope of the present invention.

As another example of the operation of this invention and referring to FIGURE 2, ammonia base spent sulphite liquor having solids content of about 10 percent was introduced into the cell shown in FIGURE 2, the liquor being fed to the liquor frames 113, 113' and 113''. An electrical potential was established between the anode 105 and the cathode 107 so as to provide a current density in the cell of about 30 milliamperes per square centimeter of area of the membrane. The feed liquor had a nitrogen content of about 4 grams per liter. The cation concentrating solution, to the catholyte frames 117, 117' and 117'' included ammonia and had a similar nitrogen content. The anion concentrating solutions include sulphur dioxide at a concentration of about 6 grams per liter. The membranes 111a, 111a' and 111a'' were selected to pass molecules having a molecular weight of less than 3000. The membranes, 111b, 111b' and 111b'' were selected to pass molecules having molecular weight of less than 1000. The membranes 111c, 111c' and 111c'' were chosen to pass molecules having a molecular weight less than about 200. As a result, the anion concentrating frames 109a, 109a' and 109a'' held a substantial portion of the lignin molecules having molecular weight between about 1000 and 3000, whereas the anion concentrating frames 109b, 109b' and 109b'' held lignin molecules having molecular weights of between 1000 and 200 and the anion concentrating frames 109c, 109c' and 109c'' primarily comprised sulphur dioxide, sugars, and other low molecular weight compounds in solution.

The various solutions in the anion concentrating frames have particular utility in certain fields and for various purposes. In this connection, the higher molecular weight anions have excellent dispersing properties in oil well drilling muds, and these anions also provide unusual binding properties for ores. In addition, the higher molecular weight fractions gel more rapidly either spontaneously or with the aid of gelling agents such as dichromate salts. The low molecular weight lignin fractions have improved oxidation characteristics and also have improved resin forming characteristics. Thus, the unit provides products with unique characteristics.

In a cell having but one treating frame, about 90 percent of the current is utilized in overcoming the resistance of the electrodes thereby providing inefficiency of operation. On the other hand, in a cell comprising three treating frames only about 20 percent of the current is consumed in overcoming the resistance of the electrodes. It is obvious that the stacking of treating frames with the use of the barrier frames provides a very substantially improved operation.

The various features of this invention which are believed to be new are set forth in the following claims.

What is claimed is:

1. In a process for the electrodialytic treatment of spent sulphite liquor to recover acid ions therefrom, providing ionizable aqueous solutions in successive positions, said aqueous solutions comprising an anion concentrating solution, a spent sulphite liquor to be electrodialyzed, a cation concentrating solution, and a barrier solution com-

prising sulphurous acid, establishing a direct current electrical potential across said aqueous solutions, and placing selective dialysis membranes between said solutions.

2. An electrodialysis cell comprising, an anolyte frame, a catholyte frame, at least two treating frames disposed between said anolyte and said catholyte frames, and a barrier frame disposed between adjacent treating frames, each treating frame including an anion concentrating frame, a cation concentrating frame and a liquor frame disposed therebetween, each said liquor frame having electrodialysis membranes on each side thereof of which at least one membrane is a non-selective electrodialysis membrane, said barrier frame having ion-selective electrodialysis membranes on each side thereof.

3. An electrodialysis cell comprising, an anolyte frame, a catholyte frame, at least two treating frames disposed between said anolyte and said catholyte frames, and a barrier frame disposed between adjacent treating frames, each treating frame including an anion concentrating frame, a cation concentrating frame and a liquor frame disposed therebetween, said liquor frame having electrodialysis membranes on each side thereof of which at least one membrane is a non-selective electrodialysis membrane, said barrier frame having ion-selective electrodialysis membranes on each side thereof, one of said ion-selective electrodialysis membranes permitting passage of anions into the cation concentrating frame of one of said treating frames and the other ion-selective electrodialysis membrane permitting passage of cations into the anion concentrating frame of another of said treating frames.

4. An electrodialysis cell comprising, an anolyte frame, a catholyte frame, at least two treating frames disposed between said anolyte and said catholyte frames, and a barrier frame disposed between adjacent treating frames, each treating frame including an anion concentrating frame, a cation concentrating frame and a liquor frame disposed therebetween, said liquor frame having a cation-selective electrodialysis membrane on the side adjacent said cation concentrating frame and having a non-selective electrodialysis membrane on the side adjacent said anion concentrating frame, said barrier frame having ion-selective electrodialysis membranes on each side thereof, one of said ion-selective electrodialysis membranes permitting passage of anions into the cation concentrating frame of one of said treating frames and the other ion-selective electrodialysis membrane permitting passage of cations into the anion concentrating frame of another of said treating frames.

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