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2009/04731 6 September 2009 (06.09.2009) ZA(71) Applicant (for all designated States except US): **EARTH METALLURGICAL SOLUTIONS (PTY) LIMITED** [ZA/ZA]; 1 Brakpan Road, Unit 72 Van Dyk Secure Business Park, Boksburg Industrial East, 1459 (ZA).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **HOWARD, Darryl** [ZA/ZA]; 13 West Cliff Drive, Parkview, 2193 Johannesburg (ZA). **GROBLER, Christo** [ZA/ZA]; No 9 Balisani, Lessing Street, Rynfield, 1501 (ZA).(74) Agent: **VON SEIDELS**; Intellectual Property Attorneys, P.O. Box 440, Century City, 7446 Cape Town (ZA).

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(54) Title: APPARATUS FOR THE TREATMENT OF AN EFFLUENT

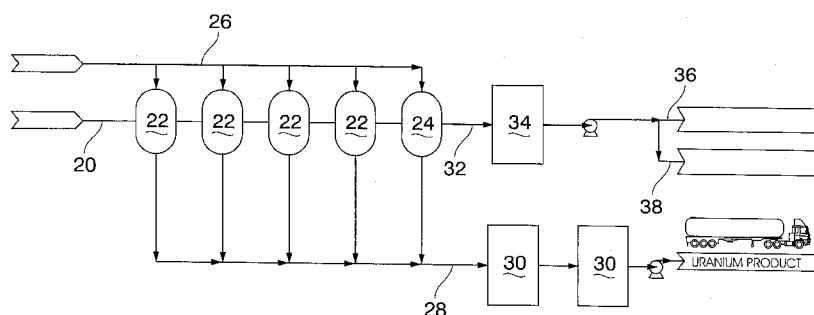


Figure 2

(57) Abstract: A process for the treatment of an effluent is provided and includes the steps of removing entrained solids and organic compounds from the effluent, preferably by means of filtration; removing uranium from the effluent using a strong base anion resin; removing cations from the effluent using a strong acid cation resin and eluting the resin with nitric acid to provide a cation eluate; removing anions from the effluent using a weak base anion resin and eluting the resin with ammonium hydroxide to provide an anion eluate; neutralising and evaporating the cation eluate to obtain a 50% mixed metal nitrate solution; and neutralising and evaporating the anion eluate to obtain substantially dry ammonium salt. The process results in the economic production of water, a uranium solution, a mixed metal nitrate solution and an ammonium salt from a hazardous waste product.

A PROCESS FOR TREATING AN EFFLUENT

5 FIELD OF THE INVENTION

The invention relates to a process for treating an effluent, more particularly an effluent containing uranium.

10 BACKGROUND TO THE INVENTION

PCT patent application number PCT/IB2007/000335 discloses a method of treating acid mine drainage (AMD) using ion exchange. The process disclosed in that application is not suitable for use with effluents that have
15 been pre-treated by addition of limestone and/or lime. The effluent obtained from such pre-treatment contains significantly reduced levels of traditional mining pollutants such as iron, aluminium, magnesium and sulphates. However, these effluents require additional treatment to meet discharge standards or potable water standards. Also, many of these effluents contain
20 uranium which is valuable and can contribute significantly to process economics if it can be recovered in a suitable form. Reverse osmosis presents a solution to this problem but there is significant production of waste in the form of brines from this process.

25 A further problem with uranium in acid mine drainage from gold mines is that it forms an ionic complex with other ions present in solution, most likely sulphates. This anionic complex of uranium is in equilibrium with uranium in the cationic form and the two species co-exist in an unknown ratio. Other metal cations, such as manganese, cobalt, nickel and copper, are also
30 present in the acid mine drainage and adsorb strongly with the cationic uranium onto a cationic resin if prior art ion-exchange processes are used to treat the effluent. This complicates separation of the other potentially valuable metals.

Ion exchange systems operate on well-known principles and include the steps of adsorbing or loading ions from an influent onto resin beads and subsequently desorbing or eluting the ions from the beads using an eluate.

5 Hereafter the adsorption step is repeated and so on.

A major shortcoming of fixed-bed systems is the cross-contamination from the diffusion that occurs at the liquid-liquid interfaces between the two primary ion exchange steps of adsorption and desorption. At the start of a
10 changeover the column is filled with solution from the ending cycle (end-solution). The end-solution is usually displaced from the column by start-solution from the following cycle. The displaced end-solution is usually routed to an appropriate storage for a repeat of the adsorption cycle.

15 Some diffusion takes place between the two liquid phases as the interface between the end-solution and start-solution progresses through the resin bed towards the column exit. This results in an uncontrolled blending of the chemical constituents of the end- and start-solutions. The extent of the cross-contamination is a function of direction of changeover from adsorption to
20 desorption or *vice versa*, process configuration with respect to concentration gradients and the application environment, for example, industrial chemical or metallurgical, effluent treatment for discharge, demineralisation to ultra-pure water, and the like.

25 A further problem occurs with fixed bed systems. At the end of desorption (regeneration) cycle the column void is filled with eluent solution containing compounds of desorption, that is concentrations of the reagents of elution and eluent salts. A column may only be introduced back into the adsorption cycle when the compounds of desorption have been fully removed from the
30 resin bed.

It is common practice to flush freshly regenerated columns with large quantities of influent solution until acceptable removal of the compounds of

regeneration has been achieved. The flushing solution is usually returned to an appropriate influent storage for retreatment. This practice reduces the net throughput of the system by the volume of flushing solution required. The sizing of the processing equipment must be correspondingly increased to
5 allow for the retreatment of the recycled flushing volume and this has significant negative capital and operational cost implications.

Still further, fixed-bed ion exchange demineralization is limited in the level of demineralization that may be achieved in a single step. High total dissolved
10 solids (TDS) (>5,000 ppm TDS) solutions usually require multiple steps of cationic and anionic treatment to achieve near-complete demineralization. The number of steps required is a function of the "equivalents" in solution, which determines the rate of ion exchange and thus the peak levels of acidity or basicity achieved before equilibrium pH points are reached. Multiple ion
15 exchange steps increase the capital cost requirement and the complexity and control of the demineralization process and it is thus desirable to limit the number of ion exchange steps as far as possible.

20 **OBJECT OF THE INVENTION**

It is an object of this invention to provide a process for treating and effluent which will at least partially overcome some of the abovementioned problems.

25 It is also an object of this invention to provide methods of operating ion-exchange systems which will enhance their efficiency.

SUMMARY OF THE INVENTION

A process for the treatment of an effluent which has been treated with either or both of limestone and lime which includes

- 5 removing entrained solids and organic compounds from the effluent;
removing uranium from the effluent through ion-exchange using a strong base anion resin;
removing cations from the effluent through ion-exchange using a strong acid cation resin and eluting the resin with nitric acid to provide a cation eluate;
- 10 removing anions from the effluent through ion-exchange using a weak base anion resin and eluting the resin with ammonium hydroxide to provide an anion eluate;
evaporating the cation eluate to obtain a concentrated mixed metal nitrate solution; and
- 15 neutralising the anion eluate to obtain an ammonium salt solution.

- Further features of the invention provide for solids to be removed by filtration and organics with activated carbon; for the cation eluate to be neutralised with any one of lime, limestone and ammonia prior to concentration; for the
- 20 cation eluate to be concentrated to 50%; for the anion eluate to be neutralised with sulphuric acid; and for the neutralised anion eluate to be evaporated to obtain substantially dry ammonium salt.

- The invention also provides a method of operating a fixed bed ion-exchange
- 25 system to reduce mixing of solutions of consecutive cycle streams which includes displacing all the solution of a first cycle stream from the ion-exchange bed until the bed is filled with a gas, and then displacing the gas with solution from the subsequent cycle stream.

Further features of the invention provide for the solution from the first cycle to be displaced with gas, preferably air, under pressure; alternately for the solution from the first cycle to be drained from the bed and replaced by gas, preferably air.

5

The invention further provides a method of operating a fixed bed ion-exchange system to avoid contamination of a cycle stream by a preceding cycle stream which includes rinsing the ion-exchange bed with a plurality of volumes of rinse solution, each volume being equal to or greater than the bed
10 void volume, and then introducing the cycle stream solution into the bed.

Further features of the invention provide for three volumes of rinse solution to be used; for at least part of the rinse solution of the first rinse volume to be removed after rinsing and to be replaced by rinse solution from the
15 subsequent rinse volume; and for rinse solution in the last rinse volume to be at least in part replaced with fresh rinse solution.

The invention still further provides a method of reducing the number of fixed bed ion-exchange units for treating a high total dissolved solids (TDS)
20 solution which includes diluting the high TDS solution to a concentration low enough for complete demineralization to be achieved in a single step.

Further features of the invention provide for the high TDS solution to be diluted with water; and for the water to be obtained from that produced by the
25 ion-exchange units.

BRIEF DESCRIPTION OF THE DRAWINGS

30 The invention will now be described, by way of example only with reference to the accompanying representations in which:

- Figure 1 is a flow diagram of an effluent filtration process;
- Figure 2 is a flow diagram of a uranium removal process;
- Figure 3 is a flow diagram of a cation removal process;
- Figure 4 is a flow diagram of a product stream concentration process
- Figure 5 is a flow diagram of an anion removal process;
- Figure 6 is a flow diagram of a further product stream concentration process;
- Figure 7 is a diagram of an ion-exchange column; and
- Figure 8 is a diagram of a process for treating high TDS solutions.

DETAILED DESCRIPTION WITH REFERENCE TO THE DRAWINGS

- 15 A process for the treatment of an effluent is provided and includes the steps of:
- removing entrained solids and organics from the effluent, preferably by means of filtration;
- removing uranium from the effluent using a strong base anion resin;
- 20 removing cations from the effluent using a strong acid cation resin and eluting the resin with nitric acid to provide a cation eluate;
- removing anions from the effluent using a weak base anion resin and eluting the resin with ammonium hydroxide to provide an anion eluate;
- neutralising and evaporating the cation eluate to obtain a 50% mixed metal
- 25 nitrate solution;
- and neutralising and evaporating the anion eluate to obtain a substantially dry ammonium salt.

Each of these steps is described in more detail below.

In this embodiment the effluent stream has the composition shown in Table 1.

5

Table 1

Effluent Stream Composition

Component	Units	Amount
Sulphate	mg/l	960
Nitrate	mg/l	4.5
Phosphate	mg/l	0
Chloride	mg/l	85
Fluoride	mg/l	0
Bicarbonate	mg/l	0.00
Carbonate	mg/l	0.00
Calcium	mg/l	245
Magnesium	mg/l	98.00
Sodium	mg/l	205.0
Potassium	mg/l	5
Strontium	mg/l	0
Ammonium	mg/l	0
Silica	mg/l	0
Manganese	mg/l	0.115
Aluminium	mg/l	0.228
Uranium	mg/l	0.12
TDS	mg/l	1603

10 Filtration of Ion-Exchange Feed

Solids and organic materials are deleterious to the ion-exchange process and are must thus be removed from the effluent feed (1). In this embodiment, sand filters (3) are used for clarification of the effluent and activated carbon columns (5) for the removal of organic materials therefrom.

15

In this embodiment, the feed stream (1) is split to feed two parallel banks of sand filters (3). Build up of solids in the sand beds is controlled by periodic

backwashing (7). Backwash slurry (9) is concentrated in a settling tank (10) and returned to the mine process plant (not shown). The filtrate (11) is passed through columns (5) charged with granular activated carbon to remove traces of organic materials.

5

When spent, the granular activated carbon is removed and replaced with a fresh charge. The spent carbon can be used to supplement the carbon fuel used for water evaporation in the elution product concentration steps described below.

10

As the filters (3) do not have the benefit of chemical regeneration for controlling bacterial growth it is necessary to continually dose a bacterial disinfectant into the feed stream (1). Low levels of dissolved chlorine are maintained by dosing hypochlorite solution (12) made up from granulated chlorine (calcium hypochlorite) (13) and ion-exchange effluent water (15) to the feed (1). If desired, treatment with lye solution (17) can be used as a back-up measure.

20 **Uranium Removal**

As shown in Figure 2, after filtration the effluent (20) is fed in two parallel streams to a set of four uranium ion-exchange columns (22) arranged in a lead-lag configuration with a fifth column (24) for polishing. At any given time one of the columns will be out of the loading cycle and subject to elution.

A strong-base anion resin is used in the columns (22, 24) to remove uranium from the solution. This process step removes the anionic uranium complex from solution which results in the cationic uranium simultaneously converting to the anionic form to maintain the equilibrium ratio. This continues until the combined concentration of the cationic and anionic species of uranium is less than 1 ppb. In this manner the uranium is isolated from the other metal cations and reduced to very low levels by targeting the anionic species.

In this instance, sulphuric acid (26) is used for elution of uranium loaded on the resin. The uranium-bearing eluate (28) is held in storage tanks (30) prior to shipping to uranium processors.

The uranium barren solution (32) reports to a storage tank (34). A portion of this solution forms the feed (36) to the cation ion-exchange system. The remainder (38) is diverted to be combined with final ion-exchange barren before discharge. This allows an election to be made between partial demineralisation of the entire process stream or near complete demineralisation of part (36) of the stream and blending the untreated remainder (38) so that the average composition of the blended product meets the required final water quality.

15

Cation Ion-Exchange

As shown in Figure 3, the cation ion-exchange system includes four fixed bed ion-exchange columns (40) filled with a strong-acid ion-exchange resin (42) which removes cations from the effluent feed (36) Three columns are in the loading cycle and one in elution at any given time.

The loading of cations onto the resin displaces protons into the solution. This enables pH to be used to control the loading cycle as the termination of cation loading is registered as an increase in solution pH. When this occurs the column is taken out of the loading cycle and the solution is drained by gravity and using air (44) for positive displacement of the solution. This process forms an important efficiency improving step and is described in more detail below under the heading "Cycle Changeover".

30

shown in Figure 5, four fixed-bed ion-exchange columns (64) are used and at any one time three are in the loading cycle and one in elution.

5 The conductivity of the exiting solution (66) is used to control the loading cycle as the termination of anion loading is registered as an increase in solution conductivity. When this occurs the column is taken out of the loading cycle and the solution is drained by gravity and using air displacement as described in more detail below under the heading "Cycle Changeover".

10 The exiting solution (66) is substantially demineralised water and can be further used as desired. In most instances the water is potable and represents a valuable commodity.

15 The loaded resin is eluted with diluted aqueous ammonia solution (68) made up from weaker solutions (70) from prior elutions and concentrated ammonia (72) from storage.

20 The concentrated portion (74) of the eluate stream exiting the columns (64) is neutralised with sulphuric acid (76) and the product stream (78) then advanced to product concentration. The weaker portions (the ends of the characteristic bell-shaped eluate concentration profile) are recycled as indicated above. In this way reagent usage and concentration of the final eluate are maximised.

25 Referring to Figure 6, the product stream (78) is concentrated further to 40% moisture by evaporation using a stream of hot gas (80) in counter-current flow to the solution introduced via spray nozzles (82) into the top of an evaporation tower (84). The concentrated product (86) is pumped continuously from the sump at the bottom of the tower via a chamber filter
30 press (88) to remove coal-based solids to a spray drier (90) where the remaining water is evaporated leaving anhydrous ammonium sulphate (92). This is then packaged (94) prior to dispatch.

The loaded resin is eluted with diluted nitric acid solution (46) made up from weaker acid solutions (48) from prior elutions and concentrated nitric acid from storage (50).

- 5 The concentrated portion of the eluate stream (52) exiting the columns (40) is further concentrated and the weaker portions (the ends of the characteristic bell-shaped eluate concentration profile) are recycled as described above. In this way reagent usage and concentration of the final eluate are maximised.
- 10 The eluate stream (52) may be neutralised with either lime or limestone or with ammonia (54) depending on whether a calcium nitrate or ammonium nitrate is desired in the stream. As shown in Figure 4, after neutralising the free acid content of the stream it is concentrated to 50% moisture by evaporation using a stream of hot gas (55) in counter-current flow to the
- 15 solution introduced via spray nozzles (56) into the top of the evaporation tower (57). The concentrated product (58) is pumped continuously from the sump at the bottom of the tower via a chamber filter press (59) to remove coal-based solids prior to dispatch.
- 20 This stream (58) contains alkali metal nitrate salts (calcium, magnesium, potassium and sodium) and proves useful as an oxidizer-stabiliser for ammonium nitrate emulsion explosives. As such, this stream has good commercial value and does not require further processing to separate out individual metal salts.
- 25 After passing through the columns (40) the cation barren effluent (60) reports to the anion exchange system.

30 **Anion Ion-Exchange**

The anions in the effluent solution (60) (which are typically primarily sulphates) are removed using a weak-base anion exchange resin (62). As

The process of the invention results in the production of water, a uranium rich solution, a mixed nitrate solution and ammonium sulphate from an environmentally hazardous waste. All the products of the process have value and are obtained in a cost effective manner which enables the waste to be
5 treated on a profitable basis.

The process of the invention is particularly effective in that it separates substantially all the uranium out of the effluent in the initial ion-exchange step which targets only the anionic uranium complexes. This avoids further
10 complicated separation processes being required to separate the cationic uranium species from the other cationic metals in solution.

The process of the invention results in a significant increase in product concentration and a reduction in elution reagent consumption. It will be
15 appreciated that many other embodiments of a process exist which fall within the scope of the invention, particularly as regards the process parameters and equipment used.

As indicated above, the process used to elute the loaded resin used in the
20 ion-exchange columns provides important advantages over prior art process. In particular, the cycle changeover procedure and rinsing procedure avoid excessive contamination of process streams and add significantly to the efficiency of the processes.

25

Cycle Changeover

Referring to Figure 7, a fixed-bed ion-change system usually includes a column (100) filled with resin (102) in the form of beads. An influent stream
30 (104) enters the column (100) at its top and exits (106) at the bottom. The eluent stream (108) enters at the bottom and exits (110) at the top. This configuration can of course be reversed. Normal cycles of the ion-exchange column alternate between influent being fed to the column to allow adsorption

or loading of ions onto the resin, and the eluent being fed to the column to achieve desorption or stripping of the ions from the resin and to so regenerate the resin and allow a subsequent loading cycle to take place.

- 5 Inter-cycle cross-contamination of the adsorption (influent) and desorption (eluent) streams occurs due to mixing of the streams at cycle changeovers.

According to the invention inter-cycle cross-contamination is significantly reduced by displacing all the end of cycle solution from the column void with
10 a gas prior to introducing solution from the subsequent cycle into the column. In this way a liquid-liquid interface is avoided and cross-contamination prevented.

In a preferred embodiment, dry and oil-free compressed air (112) is
15 introduced into the freeboard void above the resin bed and the bottom column exit (114) is routed to an appropriate storage. The end of cycle solution of the first cycle is now pushed out of the column through air displacement before the subsequent cycle solution is introduced into the column. This completely eliminates contact between the two solutions and
20 significantly reduces the cross-contamination common to all fixed-bed ion exchange systems.

The procedure is simply repeated for each subsequent cycle changeover. It will be appreciated that the solution from the first cycle could simply be
25 drained from the bed by a pump or through gravity and replaced by gas, preferably air, which enters through an appropriate valve on the column. Once the column is completely drained and the first cycle solution replaced by the gas, the subsequent cycle solution is introduced into the column and gas in the column permitted to escape through a vent valve (116) at the top
30 of the column.

This innovation shall be referred to as "blow-down" and is implemented in operation of an ion-exchange column as shown in steps 2 and 6 in Table 2

which describes the key process stream operations in controlling an ion-exchange column according to the method of the invention.

5

Table 2
Ion-Exchange Column Operation

Step	Description	Direction	Source	Destination	Control	Comment
1	Adsorption (loading)	Down-flow or up-flow	Influent Tank	Effluent Tank	Breakthrough ions measured	Saturated column to be eluted
2	Blow-down	Down-flow	Air	Influent Tank	Flow switch	Remove influent from column
3	Refill with eluate	Up-flow to de-air bed	Eluate Tank	Air Vent	Flow switch	Solution exits vent and triggers switch
4	Product elution	Down-flow	Elution Feed Tank	Product Tank	Tank level control	Elution complete at target volume
5	Elution to equilibrium	Down-flow	Elution Feed Tank	Elution Recovery	pH control	Ends when within target pH range
6	Blow-down	Down-flow	Air	Elution Recovery	Flow switch	Remove eluent from column
7	Refill with influent	Up-flow to de-air bed	Influent Tank	Air Vent	Flow switch	Solution exits vent and triggers switch
8	Flush column	Down-flow or up-flow	Influent Tank	Influent Tank	Target salt strip achieved	System cycles back to step 1.

10 Two critical issues need to be managed accurately for the blow-down system to function properly. Firstly, all of the liquid in the void space (space within a

column above and between ion-exchange resin beads) inside the column must be displaced with air (air-to-liquid) when the end of cycle solution is displaced out of the column. Secondly, all of the air in the void space inside the column must be displaced with start of cycle solution (liquid-to-air) when
5 the air is pushed upwards out of the column.

A number of alternative measuring techniques may be employed to verify that the procedure is executed successfully during the air-to-liquid stage. The simplest would be to use a flow-paddle switch to verify that flow from the
10 bottom exit has stopped thereby assuming that all end of cycle solution has been removed from the column. Alternately a flow-totaliser may be used to verify that a certain minimum of solution has been displaced from the column. Further alternately the displaced end of cycle solution may be collected in a storage tank where a level detector may be used to verify that a certain
15 minimum volume of end of cycle solution has been displaced from the column. A more intelligent system would consider that the void volume inside the column would vary depending on the adsorbed or desorbed state of the resin. Ion-exchange resins generally expand or contract depending on their chemical state and this will affect the void volume and therefore the
20 volume of cycle solution displaced by air.

When the air inside the column is displaced upwards out of the column by the start of cycle solution of the subsequent cycle, a number of alternative measuring techniques may be employed to verify that the procedure is
25 executed successfully. Similarly to those described above, these include a liquid float or flow-paddle switch on the air vent outlet to verify that the displacing solution has reached the top of the column and the air has been removed from the ion-exchange resin bed. Alternately a flow-totaliser may be used to verify that a certain minimum of start of cycle solution has been
30 introduced into the bottom of the column. Further alternately the displacing start of cycle solution may be obtained from a storage tank where a level detector may be used to verify that a certain minimum volume of solution has

been pumped from the storage tank to the column. More intelligent systems which consider the void volume inside the column can also be used.

Other modifications may be needed to make the blow-down system function properly on large scale operations. Resin beds tend to trap pockets of air and these may be difficult to remove. Air pockets inside the resin bed reduce the resin's working capacity and these must be prevented as far as possible. Entrapped air may be removed by vibrating the column with a pneumatic or electrical vibrator to collapse the resin bridging and allow trapped air to escape upwards to accumulate in the freeboard space above the resin bed within the column. Alternately, pulsed up-flow agitation of the resin bed could be used to achieve a similar effect. As a further alternative, tangential high-pressure water inlets jets installed in the floor of the column are also being considered to alleviate this problem. These will be arranged to fluidize and swirl the resin bed to so remove entrapped air.

It will be appreciated that many other cycle changeover processes exist which fall within the scope of the invention, particularly as regards the manner in which end of cycle solution is displaced from the column, the gas used and the process controlled.

Multi-Step Rinse

At the end of the desorption cycle (regeneration cycle) the column void is filled with eluant solution containing compounds of desorption, namely concentrations of the reagents of elution and eluant salts. A column should only be introduced back into the adsorption cycle when the compounds of desorption have been fully removed from the resin bed.

30

As indicated previously, it is common practice to flush freshly regenerated columns with large quantities of influent solution until acceptable removal of the compounds of desorption has been achieved. The flushing solution is

usually returned to an appropriate influent storage for retreatment. This practice reduces the net throughput of the system by the volume of flushing solution required. The sizing of the processing equipment must be correspondingly increased to allow for the retreatment of the recycled flushing volume and this has significant negative capital and operational cost implications.

This undesirable feature of conventional fixed-bed ion exchange is largely eliminated by the multi-step rinse method of the invention. Referring to Figure 8, the multi-step rinse employs a plurality of rinse vessels of volume at least equal to the column void volume and equipped with a suitable transfer pump and pipe manifold. In this embodiment three rinse vessels (120, 122, 124) are used. The order of rinsing is such that the contents of initial vessel (120) to be used to rinse the resin, and so the solution most contaminated with eluant solution, is sent to an eluate recovery tank (126) after use and replaced by the contents of the subsequent vessel (122). The contents of the final vessel (124) replace those of the second vessel (122) and the final vessel (124) then filled with clean water (128). In this way, optimal use of the rinse solution is obtained. Table 3 describes the key steps for executing a three-step rinse system but the procedure may be applied to any number of rinse steps to achieve the desired result. In the Table 3, "Tank 3" is the first rinse vessel (120), "Tank 2" is the second rinse vessel (122) and "Tank 1" the third rinse vessel (124).

This entire procedure is achieved without any modification of the column system other than adding additional routing to connect the influent and effluent manifolds of the column carousel to the multi-step rinse system as shown in Figure 8.

It will be appreciated that other methods of conducting a multi-step rinse exist which fall within the scope of the invention, particularly as regards the number of rinse cycles employed, their sequence and the manner in which rinse solution is removed and replaced.

Table 3
Ion-Exchange Column Operation

Step	Description	Direction	Source	Destination	Control	Comment
1	Blow-down	Down-flow	Air	Elution Recovery Tank	Flow switch	Remove acid from column.
2	Refill with Rinse Tank 3 solution	Up-flow	Rinse Tank 3	Air Vent	Flow switch	When air is vented solution will trigger flow switch
3	Circulate for x minutes	Up-flow	Rinse Tank 3	Rinse Tank 3	Ends when target time x is reached	This step allows equilibrium to be reached
4	Blow-down	Down-flow	Air	Elution Recovery Tank	Flow switch	Remove 1st rinse from column.
5	Refill with Rinse Tank 2 solution	Up-flow	Rinse Tank 2	Air Vent	Flow switch	When air is vented solution will trigger flow switch
6	Circulate for x minutes	Up-flow	Rinse Tank 3	Rinse Tank 3	Ends when target time x is reached	This step allows equilibrium to be reached
7	Blow-down	Down-flow	Air	Rinse Tank 3	Flow switch	Remove 2nd rinse from column.
8	Refill with Rinse Tank 1 solution	Up-flow	Rinse Tank 1	Air Vent	Flow switch	When air is vented solution will trigger flow switch
9	Circulate for x minutes	Up-flow	Rinse Tank 2	Rinse Tank 2	Ends when target time x is reached	This step allows equilibrium to be reached
10	Blow-down	Down-flow	Air	Rinse Tank 2	Flow switch	Remove 3rd rinse from column.
11	Refill with Rinse Tank 1 solution	Up-flow	Clean make-up water	Air Vent	Flow switch	When air is vented solution will trigger flow switch
12	Circulate for x minutes	Up-flow	Rinse Tank 1	Rinse Tank 1	Ends when target time x is reached	This step allows equilibrium to be reached
13	Blow-down	Down-flow	Air	Rinse Tank 1	Flow switch	Remove 4th rinse from column.
14	Refill with influent	Up-flow to de-air bed	Influent Tank	Air Vent	Flow switch	Solution exits vent and triggers switch
15	Direct transfer to adsorption cycle, no flushing water	Down-flow or up-flow	Influent Tank	Effluent Tank	Breakthrough ions measured on saturation	

Dilution Method

As indicated above, fixed-bed ion exchange demineralization is limited in the level of demineralization that may be achieved in a single step. High Total dissolved solids (TDS) (>5,000 ppm TDS) solutions usually require multiple steps of cationic and anionic treatment to achieve near-complete demineralization, the number of steps required being a function of the "equivalents" in solution. Multiple ion exchange steps increase the capital cost requirement and the complexity and control of the demineralization process.

As shown in Figure 8, according to the invention, a high TDS solution (150) feed to an ion-exchange column (152) is diluted with the addition of clean water (154) to lower the TDS level to one which is low enough to allow complete demineralization to be achieved in a single step.

This has the result that the design of a suitable plant must be adjusted to accommodate the additional flow through the single-stage cationic and anionic system.

The further problem is posed in that the process may now require large volumes of additional clean water to treat high-TDS solutions. However, this is easily resolved by obtaining the clean-water requirements from the effluent stream (156) at the back end of the demineralization process and circulating this recovered water to the front end of the process, to be blended in a carefully controlled ratio with the high TDS influent (150). In this way the system behaves like a "black box", with no external clean water requirements and high TDS influents are demineralised in a single step with ease.

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It will be appreciated that the degree of dilution will vary depending on the composition of the stream being treated and the equipment available.

CLAIMS:

1. A process for the treatment of an effluent which has been treated with limestone and/or lime which includes
5 removing entrained solids and organic compounds from the effluent;
removing uranium from the effluent through ion-exchange using a strong base anion resin;
removing cations from the effluent through ion-exchange using a strong acid cation resin and eluting the resin with nitric acid to provide
10 a cation eluate;
removing anions from the effluent through ion-exchange using a weak base anion resin and eluting the resin with ammonium hydroxide to provide an anion eluate;
evaporating the cation eluate to obtain a concentrated mixed metal
15 nitrate solution; and
neutralising the anion eluate to obtain an ammonium salt solution.
2. A process as claimed in claim 1 wherein the solids are removed by filtration and the organic compounds are removed using activated
20 carbon.
3. A process as claimed in claim 1 or claim 2 wherein the cation eluate is neutralised with any one of lime, limestone and ammonia prior to concentration.
25
4. A process as claimed in any one of claims 1 to 3 wherein the neutralised anion eluate is evaporated to obtain a substantially dry ammonium salt.
- 30 5. A process as claimed in claim 4 wherein the anion eluate is neutralised with sulphuric acid prior and ammonium sulphate obtained after evaporation.

6. A method of operating a fixed bed ion-exchange system to reduce mixing of solutions of consecutive cycle streams which includes displacing all the solution of a first cycle stream from the ion-exchange bed until the bed is filled with a gas, and then displacing the gas with solution from the subsequent cycle stream.
7. A method as claimed in claim 6 wherein the solution from the first cycle is displaced with gas, preferably air, under pressure.
8. A method as claimed in claim 6 wherein the solution from the first cycle is drained from the bed and replaced by gas, preferably air.
9. A method of operating a fixed bed ion-exchange system to avoid contamination of a cycle stream by a preceding cycle stream which includes rinsing the ion-exchange bed with a plurality of volumes of rinse solution, each volume being equal to or greater than the bed void volume, and then introducing the cycle stream solution into the bed.
10. A method as claimed in claim 9 wherein three volumes of rinse solution are used.
11. A method as claimed in claim 10 wherein at least part of the rinse solution of the first rinse volume is removed after rinsing and is replaced by rinse solution from the subsequent rinse volume.
12. A method as claimed in claim 11 wherein rinse solution in the last rinse volume is replaced at least in part with fresh rinse solution after rinsing.
13. A method of reducing the number of fixed bed ion-exchange units for treating a high total dissolved solids (TDS) solution which includes diluting the high TDS solution to a concentration low enough for complete demineralization to be achieved in a single step.

14. A method as claimed in claim 13 wherein the high TDS solution is diluted with water.
- 5 15. A method as claimed in claim 14 wherein the water is obtained from that produced by the ion-exchange units.

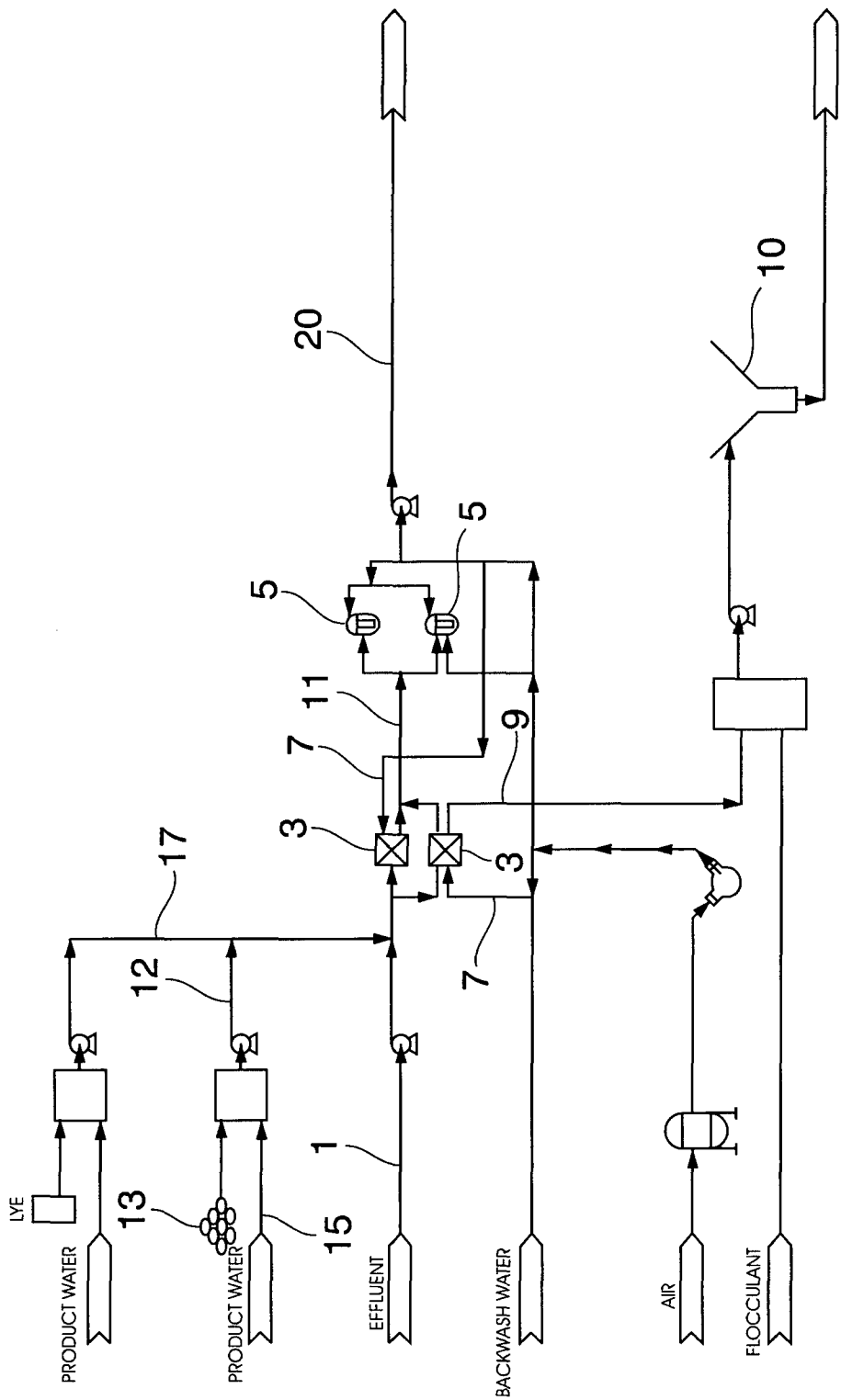


Figure 1

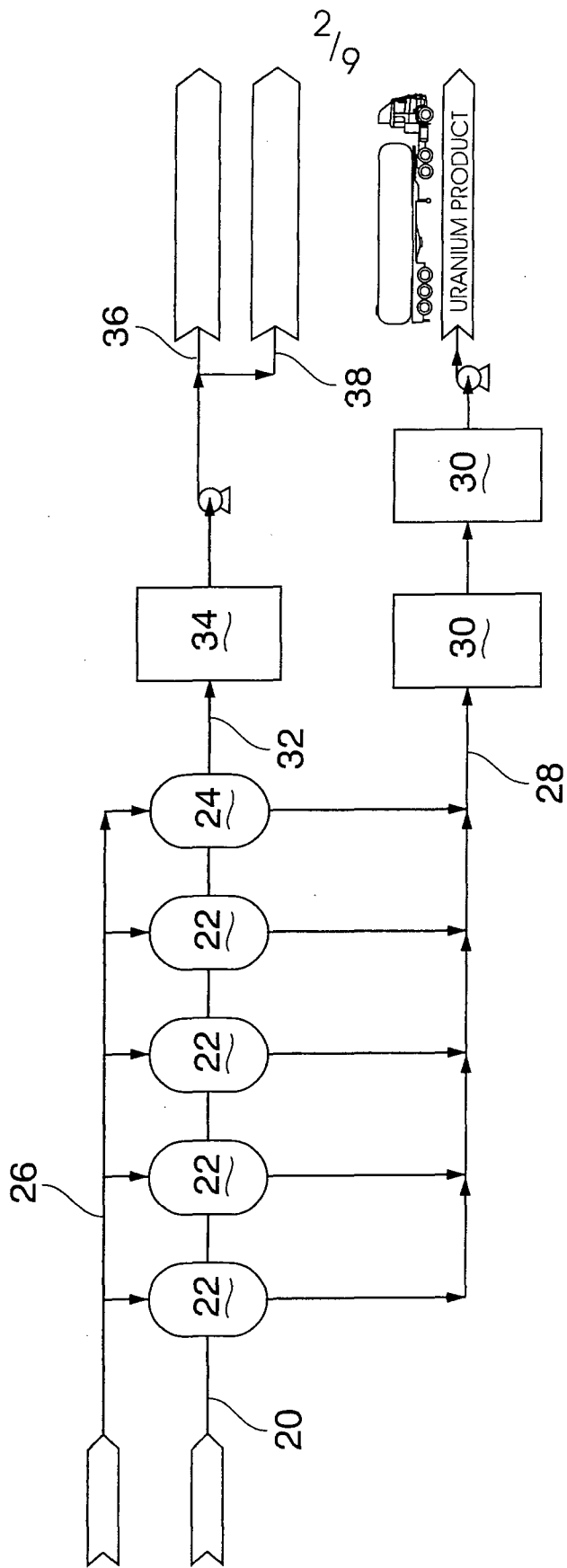


Figure 2

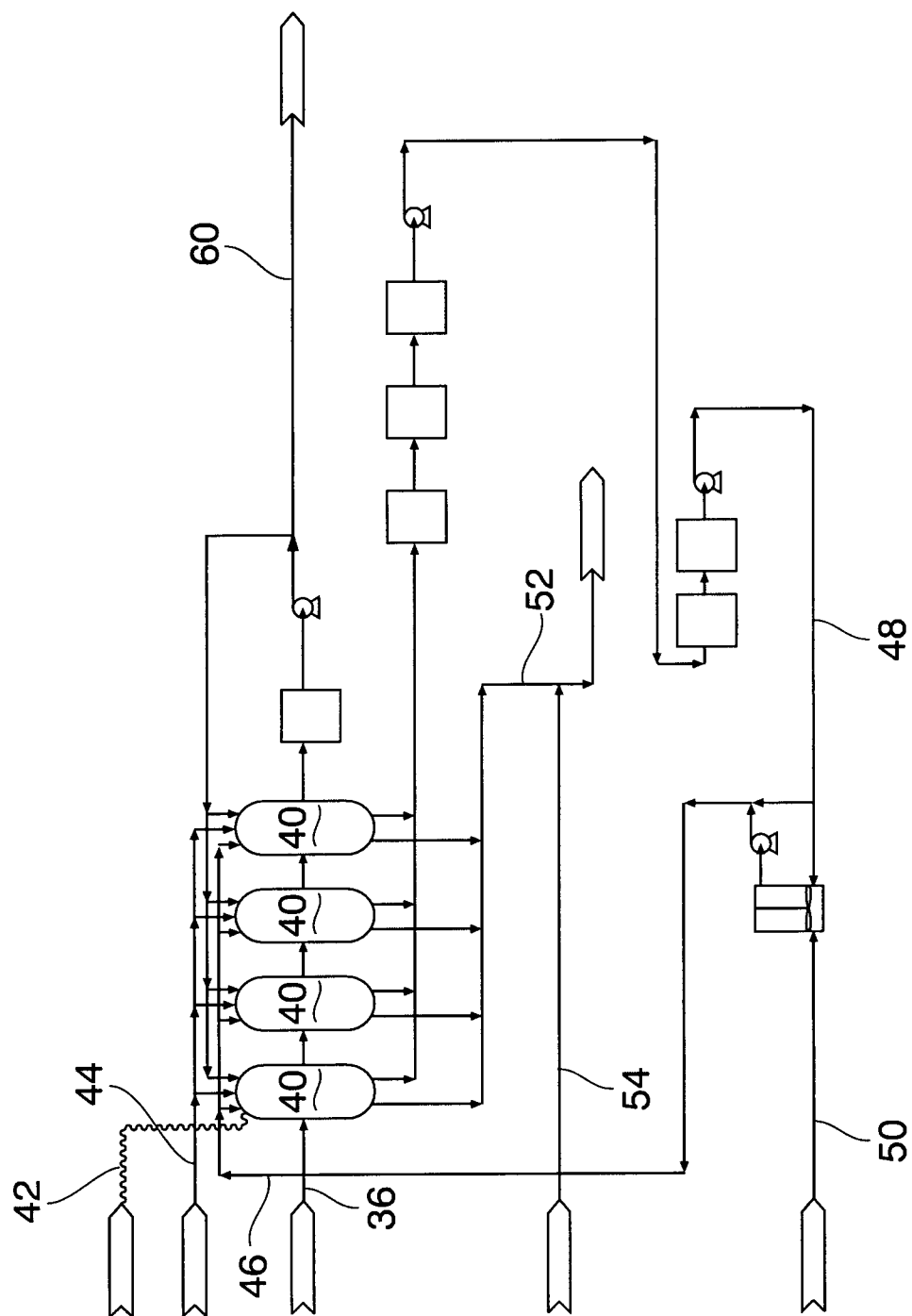


Figure 3

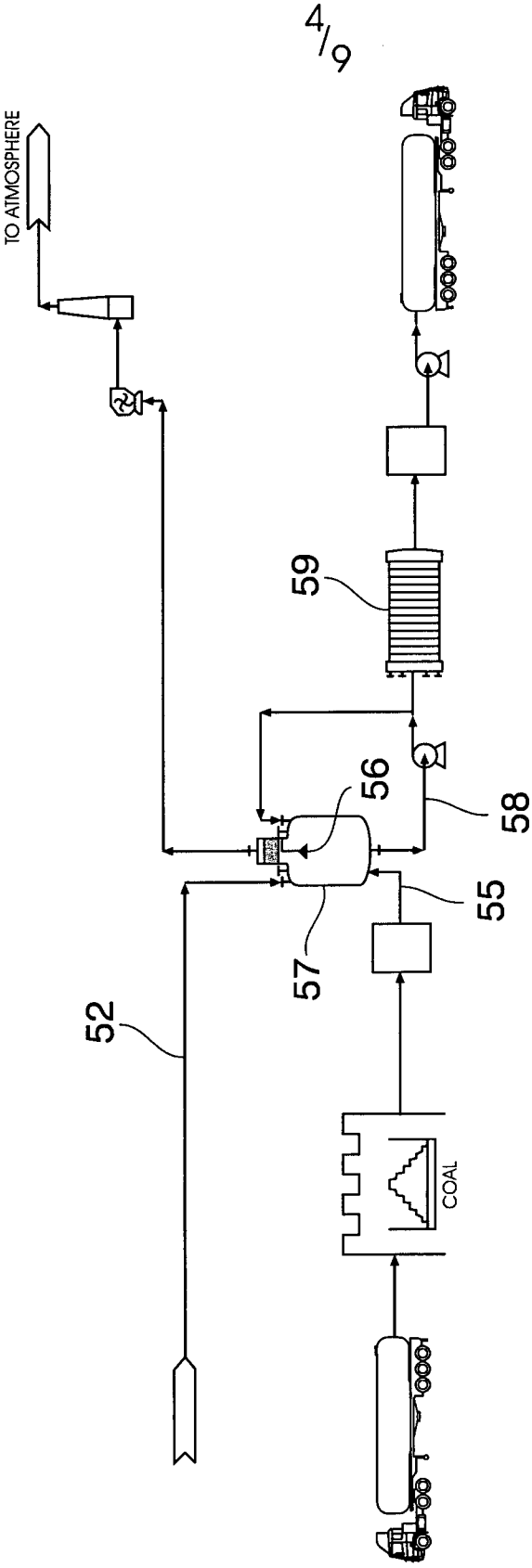


Figure 4

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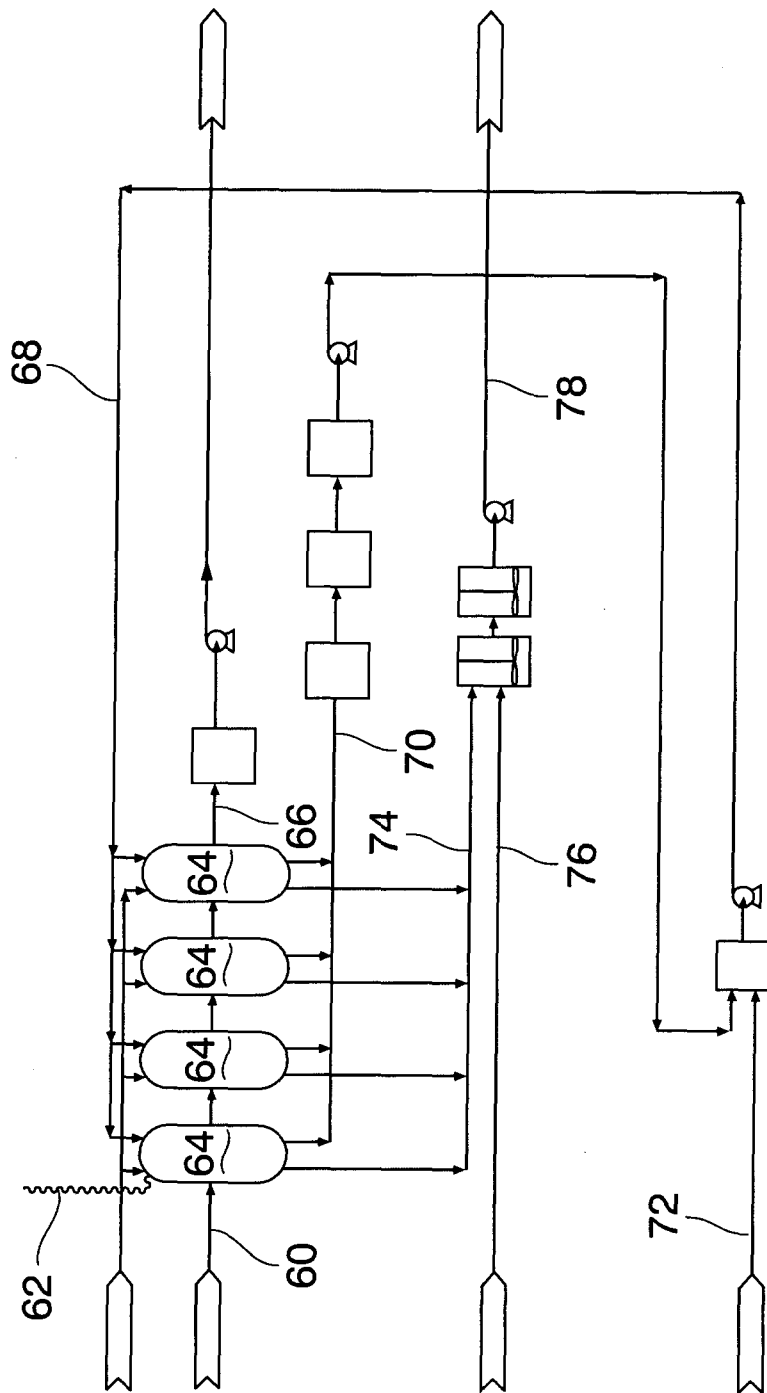


Figure 5

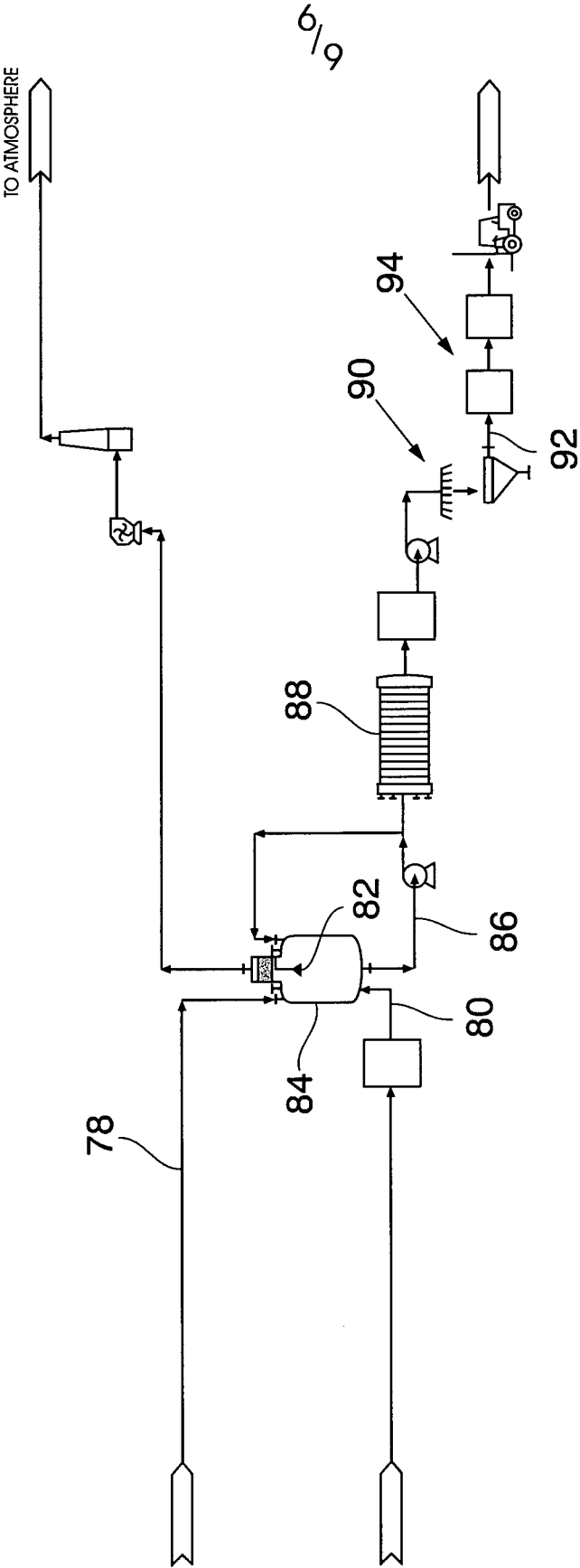


Figure 6

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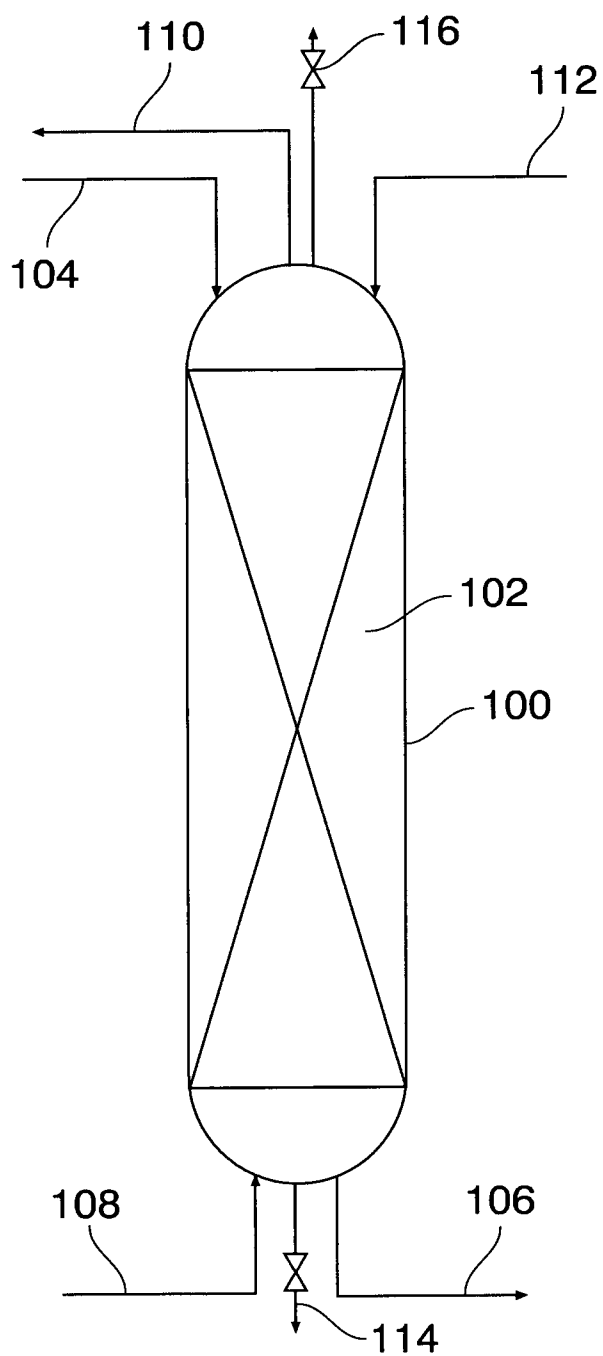


Figure 7

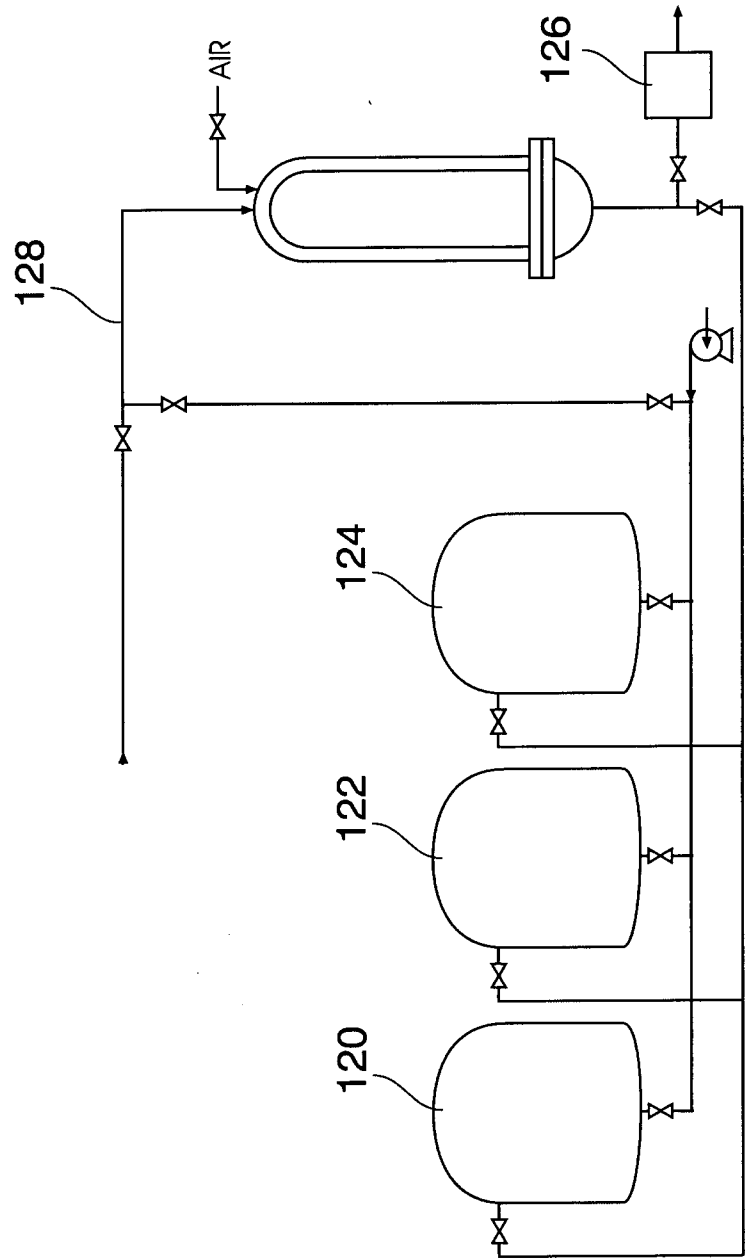


Figure 8

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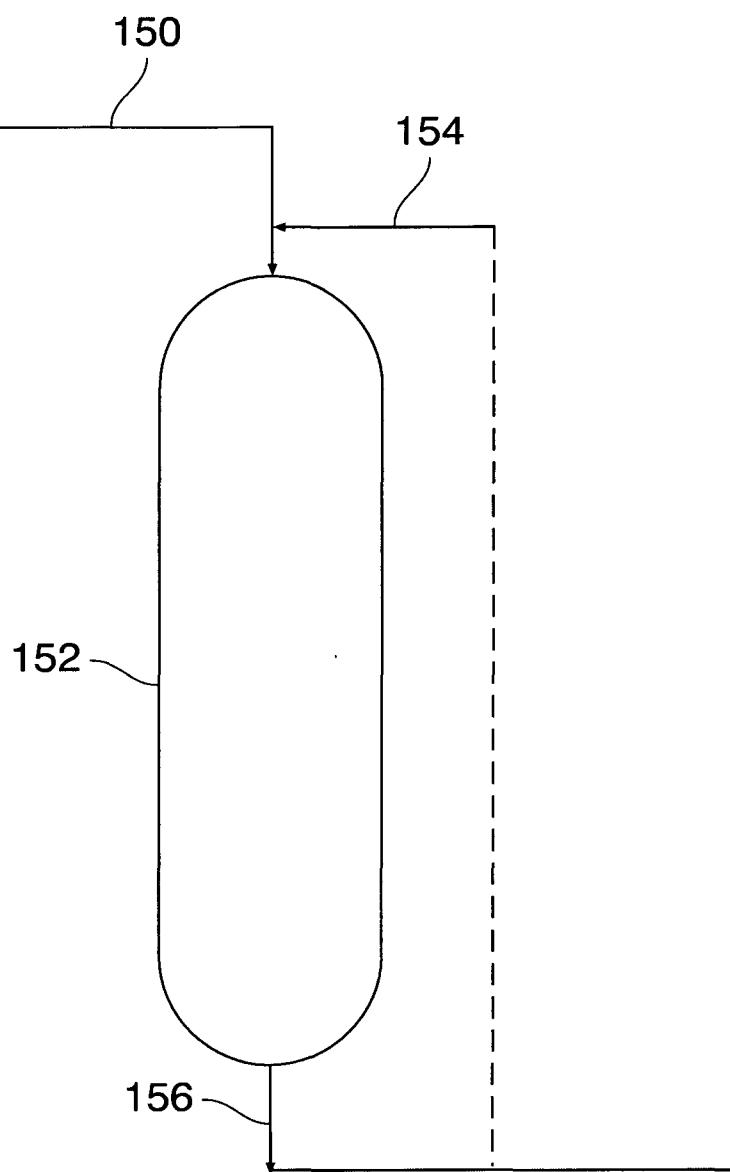


Figure 9