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(54) Methods and apparatus for treating aqueous indutrial effluent.

(57) Aqueous industrial effluent containing dissolved species which it is desired to separate from the effluent, such as valuable, poisonous or radioactive metal ions, is treated preliminarily to release gas which is, or is derived from, secondary dissolved species which tend to stabilise the desired species in solution in the effluent. The effectiveness of a subsequent separation treatment for the desired species, such as coprecipitation, ion exchange, adsorption or solvent extraction, is thereby increased.

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This invention relates to methods and apparatus for treating aqueous industrial effluent. In one particular aspect it relates to the treatment of radioactive effluent e.g. from nuclear power stations, spent fuel reprocessing plants, radioisotope handling facilities and other nuclear-related facilities. However, it may also relate to other types of industrial effluent from which it is desired to separate dissolved components.

A typical radioactive effluent contains a variety of radionuclides in aqueous solution, in volumes too large for long-term management. It is conventional to treat this effluent solution to separate out the radionuclides - typically a mixture of heavy transition metal ionsinto a more concentrated form, typically by precipitation, coprecipitation, ion exchange, adsorption or solvent extraction.

A problem is that some radionuclides, such as iodine in reprocessing effluent, are volatile and tend to be released gradually from the effluent throughout the separation process. Special measures are needed to contain and adsorb these volatile radioactive substances.

Separation processes of the type described also have relevance to other types of industrial effluent containing useful or hazardous components which it is desired to recover or remove. Examples arise in noble metal refining industry, metal plating industry and catalyst manufacture.

The conventional separation processes are effective, but clearly it would be desirable to make them still more effective.

Having investigated such effluent treatment processes, we have found that by a preliminary treatment step in which gas is released from the effluent to reduce the level of certain dissolved species therein, we can achieve practical advantages in the subsequent separation treatment wherein the primary species is removed or separated from the effluent.

In one aspect the invention provides a method of treating aqueous industrial effluent, in which a first species dissolved in the effluent is separated from the effluent by a separation treatment, characterised by a preliminary step of treating the effluent before the separation treatment to release and separate from it a gas, thereby enhancing the separation treatment by reducing the content in the effluent of a dissolved second species which stabilises the first species in solution in the effluent, said gas being, or being derived from, the second species.

This reflects an application of our findings, that typical separation treatments are hindered by the presence in the effluent of other species which tend to stabilise, e.g. by complexing, the first, desired species.

Commonly, although not exclusively, a first species is a cation and a second species an anion. Common relevant second species include oxy-anions e.g. of carbon, nitrogen and sulphur, and organic ligands.

In most important industrial contexts, a first species is a transition metal species.

The second species may be a dissolved gas, in which case the preliminary treatment may be simply to release it from the effluent. An example is carbon dioxide, which exists in solution in equilibrium with carbonate and bicarbonate ion.

Commonly, however, the second species undergoes chemical conversion to form the gas. For example, carbonates may be converted to carbon dioxide, nitrates to volatile nitrogen oxides, and iodide oxidised or iodate reduced to volatile iodine.

Accordingly, the preliminary step may comprise one or more of oxidising or reducing the second species, adjusting the pH of the effluent, heating and/or agitating the effluent, and bubbling some other gas through the effluent, to achieve the desired gas release.

In the specific context of radioactive effluent treatment, the invention provides in a further aspect a method of treating aqueous radioactive effluent in which at least one dissolved radionuclide is separated from the effluent by a separation treatment, characterised by a preliminary step of treating the effluent before the separation treatment to release and separate from it a gas, thereby reducing the level in the effluent of dissolved species other than said at least one dissolved radionuclide.

In the context of radioactive effluent treatment, it should be noted that the gas released from the effluent may itself be radioactive. In this case, the released gas should be contained, and desirably absorbed or adsorbed, to prevent its spread in the system.

In a further aspect, we provide apparatus for carrying out a method as defined above. In particular, we provide apparatus for treating aqueous radioactive effluent, comprising an enclosed vessel to hold the effluent and means for separating dissolved radionuclides from the effluent, characterised by pH adjustment means, connected to act on effluent held in the vessel, and gas uptake means for isolating gas, released from effluent held in the vessel when the pH thereof is adjusted by the pH adjustment means, from the effluent in the vessel.

Embodiments of the invention are now described by way of example, with reference to the accompanying drawings in which

Fig. 1 illustrates variation of ^{241}Am decontamination factor with concentration of dissolved carbonate;

Fig. 2 illustrates decontamination of radioactive carbon and iodine by pH adjustment;

Fig. 3 shows schematically apparatus for treating spent fuel effluent from a reprocessor;

Fig. 4 shows a different apparatus, for treating nuclear power plant effluent, and

Fig. 5 shows apparatus for treating a non-radioactive industrial effluent.

Examples of experimental work leading to the present invention are described with reference to Figs. 1 and 2.

In a first experiment, the effect of carbonate concentration on the decontamination factor (DF) of $^{241}Am^{3+}$ was investigated. A test solution, simulating a nuclear effluent, contained sodium, nitrate, carbonate and Am^{3+} ions. The solution was treated with ferrous ion and sodium hydroxide to coprecipitate Am as $Am.Fe(OH)_3$, a known coprecipitation process for Am. The precipitate was separated by filtration and the DF (the ratio between the initial and final concentrations of Am) determined for a variety of carbonate concentrations. Fig. 1 shows the result. We found that DF ^{241}Am was substantially reduced by the presence of carbonate in solution, owing to stabilisation of the Am^{3+} in solution by a complexing effect.

We found furthermore that other transition metal species had decontamination factor characteristics of a similar type, according to carbonate concentration.

In a further experiment the pH of a different test solution containing sodium cations and nitrate, iodide, hydroxy and carbonate anions was adjusted downwardly by addition of nitric acid from a starting pH above 10. As can be seen from Fig. 2, the decontamination factors of ^{14}C and ^{129}I increased for increasing reduction of the pH. The fall in pH destabilised the iodide and carbonate in solution, displacing the corresponding gases I_2 and CO_2. In this model experiment, there was one-to-one correspondence between ^{14}C and carbonate ion. Carbonate was removed effectively from the solution by reducing the pH value to below 8, and still more effectively below 6. Reduction to below 6 achieved an effective elimination of almost all of the iodine in solution.

Based on the above results, we observe that elimination of carbonate is a good way of increasing the decontamination of Am and similar species, and reducing pH is a good way of eliminating carbonate. Corresponding results can be obtained for other radionuclides, with respect to other species in solution which may have a ligand or anion complexing effect in solution, inhibiting separation of the radionuclides.

A typical radioactive effluent contains, for example, sodium ion, nitrate, sulphate and carbonate at roughly molar levels (non-radioactive species) and radioactive species such as Cs^+, Sr^+, Am^{3+}, NpO_2^{2+}, TcO_4^-, I^- and CO_3^{2-} at the order of hundredth-molar concentrations. This would reflect the history of a spent reprocessing fuel, which had been dissolved in nitric acid and then neutralised with NaOH. Carbonate may have-come from the reprocessing process, also as an impurity in NaOH. Carbon may also be present in organics such as carboxylates e.g. citrate and EDTA used in apparatus preparation. Such compounds also tend to be stabilising with respect to radionuclide species in solution.

It should be mentioned that during the actual reprocessing, gaseous iodine is given off. That does not concern the effluent processing.

Fig. 3 illustrates a method and apparatus for removing carbonate and iodine from reprocessor spent fuel effluent, using an initial pH adjustment step followed by conventional coprecipitation of radionuclides.

Reprocessed effluent 1 containing radionuclides such as ^{137}Cs, ^{90}Sr, ^{14}C, ^{237}Np and ^{241}Am is contained in a batch in an effluent processing tank 2, from previous processing indicated schematically at 3. Typical treatment volumes vary between 0.001 and 1 m^3/day, so a batch process may need to be carried out only once a day or less. A pM adjuster was introduced controllably from pM adjuster supply tank 4 into the effluent, to adjust its pM. Where the effluent pM is high, an acid such as nitric acid is a suitable adjuster. The pH is reduced to a suitably low value e.g. from 2 to 4. As a consequence, carbonate and iodine present in the effluent - including ^{14}C and ^{129}I - are evolved from the effluent as carbon dioxide and iodine gas. The effluent was stirred by an agitator 8 driven by a drive 7, to promote pH adjustment through the tank, and evolution of the released gases.

Evolved gas, containing partly radioactive CO_2 and I_2, was collected in an adjacent gas processor 6 to prevent scattering of its radioactivity into the surroundings. A suitable gas processor 6 contains a silver-based adsorbent e.g. silver alumina, to remove the iodine, and some suitable absorbent for CO_2, preferably a solid such as $CaCO_3$ or $BaCO_3$ to minimise volume.

When evolution of gas is finished, a valve 6 is closed to isolate the gas processor 6 from the effluent tank 2. Coprecipitating agent is then fed into the tank 2 from coprecipitating agent supply tank 5, to coprecipitate radionuclides. For example, conventional reagents such as sodium phosphomolybdate and ferrocyanic acid (for Cs), calcium phosphate and barium sulphate (for Sr) and ferric hydroxide and oxalate (for Np and Am) are used. The various reagents need not necessarily be added simultaneously, but it is desirable to add them in one stage to simplify the processing, provided that the conditions required for the respective coprecipitations do not differ greatly. Since the effluent is substantially carbonate-free, coprecipitation occurs with high efficiency. Again the agitator 8 is operated, to promote formation of precipitate with entrainment of radionuclide.

The effluent processing tank 2, the supply tanks 4,5 and gas processor 6 form an integrated enclosed structure, preventing escape of volatile components into the surroundings.

After precipitation, the slurry is fed from the tank 2 into a precipitate separation device 10 by a transfer pump 9. A filter, e.g. a sintered metal filter or tubular filament, is an effective separator for the precipitate. Filtered effluent gradually enters the processed efflu-

ent receiving tank 11. The precipitate, rich in radionuclides, remains on the filter to be collected for long-term management. Typically the filter is backwashed by a cleaning fluid, from cleaning fluid storage tank 12 by backwash pump 13, into a precipitate receiving tank 14. Water may be used for backwash. The smallest possible volume is used, to minimise the volume of the high-activity effluent portion.

The use of backwash to transfer high-activity precipitate is just one possibility. Mechanical removal of precipitate is also possible.

As described, the reprocessing effluent is processed into two parts: the liquid with very substantially reduced radioactivity level, and the precipitate containing most of the activity from the original effluent. The volume of the processed liquid effluent is scarcely less than the original effluent volume, but its radionuclide concentration is reduced typically to below 1% of the original value. Conversely, the concentration of radionuclide in the precipitate is more than a hundred times the concentration in the original effluent, with a volume about one hundredth the original effluent volume.

As described, the preliminary removal of carbon dioxide enhances the decontamination of Am and other transition elements showing a decontamination characteristic corresponding to that of Fig. 1. Furthermore, the concomitant removal of radioactive iodine deals with this iodine at an early stage and prevents it from volatilising and scattering to interfere with the subsequent filtering etc. processes. Consequently special iodine adsorbers are not needed at these subsequent stages.

In the process described, the pretreatment and the precipitation can be carried out in a single vessel, so simple plant can be used.

The degassing can be promoted further by heating the effluent, and/or blowing gas (e.g. air) through it in addition to adjusting the pH.

Fig. 4 shows an embodiment in which effluent from a nuclear power plant is treated. The effluent 15, containing radionuclides such as ^{137}Cs, ^{90}Sr, ^{14}C, ^{129}I and ^{60}Co, is fed from the effluent supply tank 17 of the nuclear power plant to an effluent processing tank 16. A perforated conduit 19 extends into the tank, for bubbling gas through the tank contents from a gas supply container 18. A heater 33 is also provided for heating the tank. In a preliminary treatment, the effluent is treated by bubbling gas through it to promote the volatilisation of certain components therein, such as $^{12}C/^{14}C$ and $I/^{129}I$ which volatilise as carbon dioxide and iodine respectively.

Where the initial pH of the effluent is high, an acid gas such as NO_x is appropriate for bubbling from the supply 18. It reduces the pH of the effluent, with a result as described previously. If the pH is not high, air can be used. The effect is slower, but the bubbling of air (lean in CO_2) through the richly carbonated effluent gradually reduces the carbonate by taking out carbon dioxide. The same can occur with other dissolved volatile components.

Suitable shaping of the gas conduit 19, as well as heating of the effluent, can further promote escape of volatiles.

The released gases, containing radioactive iodine and CO_2 in this case, are collected into gas processor 20 and adsorbed/absorbed as in the first embodiment, without scattering into the environment. The valve 20 is then closed to isolate the effluent from the gas processor and inhibit any tendency for redissolving.

The effluent then passes to an ion exchange column 21, for separation of the metal species. Conventional ion exchangers such as ammonium phosphomolybdate, cobalt potassium ferrocyanate and copper-impregnated zeolite ferrocyanate (for Cs), and sodium titanate and titanium phosphate (for Sr and Co) may be used. The ion exchange processes need not all be applied concurrently, but if conditions allow it is nevertheless preferred that they be all loaded into one column.

Again, the preliminary removal of dissolved carbonate relatively destabilises the mentioned metal species in solution (although not alkali and alkaline earth metal species) and improves the efficiency of the ion exchange separation.

Aqueous effluent lean in radionuclides passes from the ion exchange column 21 to the processed effluent storage tank 23. The ion exchanger operates until it starts to be exhausted, whereupon it is removed and replaced (using flanges 22). Replacement due time is assessed, in a known manner, by measuring radionuclide concentration in the liquid leaching from the column. The exhausted ion exchanger is handled as relatively high-level waste or, if it is of a reusable type, it is regenerated for re-use and the regenerative solution (containing highly concentrated radionuclide at small volume) is the high-level waste.

As with the first embodiment, it will be seen that the original effluent separates into two portions, a small-volume high-activity ion exchanger portion and a large-volume low-activity processed liquid effluent. The ion exchanger portion volume is typically less than one fiftieth of the original effluent volume.

It will be understood how the above-described embodiments both increase the efficiency of separation of radionuclides from effluent, enable a convenient process, and keep short the time spent treating a given amount of effluent.

The use of ion exchange by chromatography allows equipment to be kept small, and reduces the generation of secondary waste.

It should be understood that the features of the first two embodiments may be combined, with additional or supplementary pH adjustment and/or heating being used together with bubbling of gas.

Embodiments relating to general (non-radioactive) industrial effluents are now discussed with reference to Fig. 5.

Relevant effluents typically include useful or hazardous components which it is desired to recover/remove. Typical of such elements are Ru, Pd, Pt, Au, Cr and Cd. The apparatus is broadly similar to that in the first embodiment. Industrial effluent 24 containing components as mentioned is supplied from the effluent supply tank 26 into the effluent processing tank 25 for treatment. Taking account of the specific nature of the effluent, it is treated with oxidising or reducing agent from oxidising/reducing agent supply container 27. For example, Ce (oxidising) and Ru, Pd (reducing) may be relevant. By this means, stabilising species in the solution (and in particular anions) can be converted to relatively volatile forms which can be taken off as gas. For example, dissolved nitrates (which may stabilise dissolved platinum group species) can be rendered more volatile by reduction to nitrite and still more volatile if reduced to nitrogen monoxide. Equally, carbonate can be removed as carbon dioxide by using acidic agents. As before, an agitator 38 promotes the reactions and the evolution of the volatile products. Volatiles such as NO_x and CO_2 are discharged through gas outlet 29. According to the nature of the volatiles, it may not be necessary to isolate them from the surroundings. It is however desirable to close the gas outlet 29 by valve 29 to prevent redissolving of the removed substances when gas evolution has substantially finished.

Suitable ion exchange substances for the useful/hazardous components are fed into the processing tank 25 from an ion exchanger supply 28. Ion exchanger substances such as described in the second embodiment may be relevant. If plural they need not all be added simultaneously, but simultaneous addition is preferable.

Since stabilising anions were removed in the preceding volatilisation process, the ion exchange proceeds efficiently. The ion exchanger with the adsorbed components is then sent by slurry transfer pump 39 to separating mechanism 30, e.g. a filter (sintered metal or tubular filament) to separate the ion exchange material from the liquid effluent. Liquid effluent, separated from the ion exchanger and substantially free of the desired/dangerous component, passes gradually to the processed effluent tank 41. The ion exchange material incorporating the desired/dangerous component(s) is transferred from the separating mechanism e.g. by backwash or mechanical removal, to the ion exchanger receiving tank 32. Backwash, e.g. by water, may be from cleaning liquid tank 31 through transfer pump 43.

By the means described, the liquid effluent may be rendered into a state in which it can safely be discharged into the environment e.g. the sea or a river. Conversely, the useful or dangerous substances are concentrated into a low volume making it more efficient to recover or dispose of the materials as appropriate.

Claims

1. A method of treating aqueous industrial effluent, in which a first species dissolved in the effluent is separated from the effluent by a separation treatment,

   characterised by a preliminary step of treating the effluent before the separation treatment to release and separate from it a gas, thereby reducing the content in the effluent of a dissolved second species which stabilises the first species in solution in the effluent, said gas being, or being derived from, the second species.

2. A method according to claim 1 in which the first species is cationic and the second species is anionic.

3. A method according to claim 1 or claim 2 in which the first species is a transition metal species.

4. A method according to any one of claims 1 to 3 in which the first species is radioactive.

5. A method according to any one of the preceding claims in which the preliminary step causes chemical conversion of the second species to form said gas.

6. A method according to claim 5 in which the preliminary step comprises oxidizing or reducing the second species.

7. A method according to any one of the preceding claims in which the preliminary step comprises one or more of:

   adjusting the pH of the effluent;
   heating the effluent;
   agitating the effluent, and
   bubbling a treatment gas, different from said gas, into the effluent.

8. A method according to any one of the preceding claims, comprising absorbing or adsorbing the released gas.

9. A method according to any one of the preceding claims in which the separation treatment comprises one or more of

   precipitation;
   coprecipitation;
   ion exchange;
   adsorption, and

solvent extraction
of the first species from the effluent.

10. A method according to any one of the preceding claims in which the second species is an oxyanion or an organic ligand.

11. A method according to claim 10 in which the second species comprises carbon and the released gas comprises carbon dioxide.

12. A method of treating aqueous radioactive effluent in which at least one dissolved radionuclide is separated from the effluent by a separation treatment,
characterised by a preliminary step of treating the effluent before the separation treatment to release and separate from it a gas, thereby reducing the level in the effluent of dissolved species other than said at least one dissolved radionuclide.

13. A method according to claim 12, in which the preliminary step comprises one or more treatments selected from
adjusting the effluent pH;
oxidizing or reducing the dissolved species;
heating the effluent;
agitating the effluent, and
bubbling a treatment gas, different from said gas, into the effluent.

14. A method according to claim 12 or claim 13 in which the separation treatment comprises one or more of precipitation;
coprecipitation;
ion exchange;
adsorption, and
solvent extraction
of the at least one dissolved radionuclide.

15. A method according to any one of claims 12 to 14 in which the released gas comprises radionuclides.

16. Apparatus for treating aqueous radioactive effluent, comprising an enclosed vessel (2,16) to hold the effluent and means for separating dissolved radionuclides from the effluent,
characterised by
pH adjustment means (4,18), connected to act on effluent held in the vessel (2,16), and
gas uptake means (6,20) for isolating gas, released from effluent held in the vessel (2,16) when the pH thereof is adjusted by the pH adjustment means, from the effluent in the vessel (2,16).

17. Apparatus according to claim 16 in which the gas uptake means (6,20) comprises a gas absorber or adsorber.

18. Apparatus according to claim 16 or claim 17, comprising at least one of
means (8) for agitating effluent in the vessel (2,16);
means (19) for bubbling gas through effluent in the vessel (16), and
means (33) for heating effluent in the vessel (16).

Fig.1.

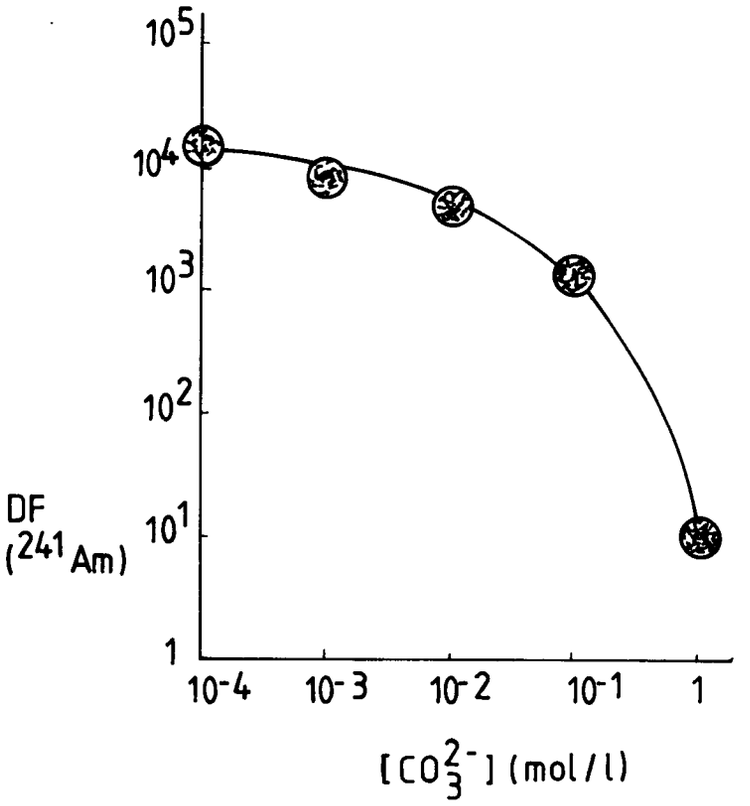
10^5
10^4
10^3
10^2
10^1
1
DF
(^{241}Am)
10^{-4}
10^{-3}
10^{-2}
10^{-1}
1
$[CO_3^{2-}]$ (mol/l)

Fig.2.

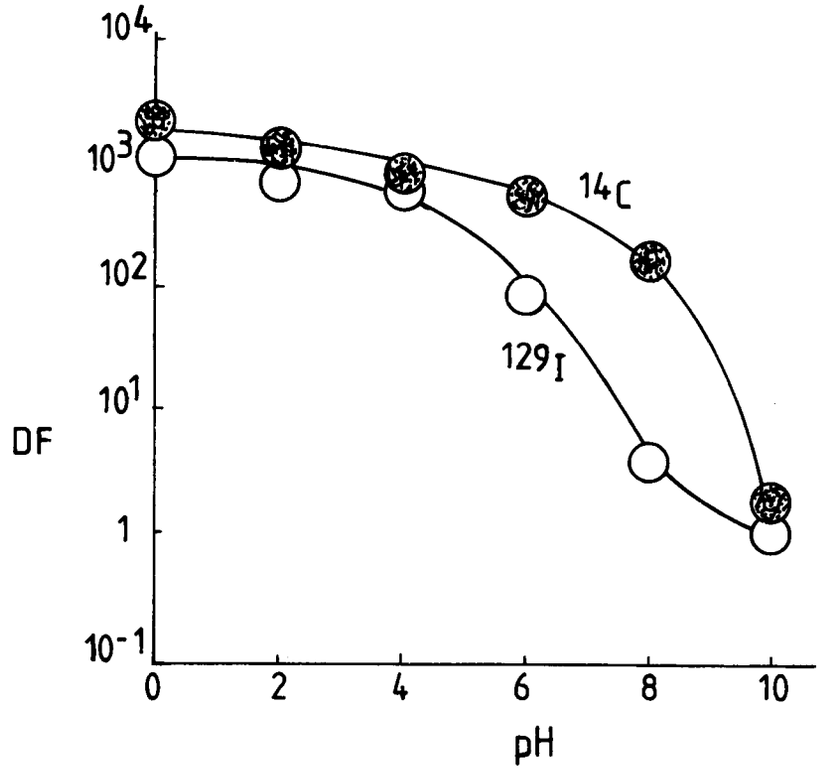
10^4
10^3
10^2
10^1
1
10^{-1}
DF
^{14}C
^{129}I
0
2
4
6
8
10
pH

Fig.3.

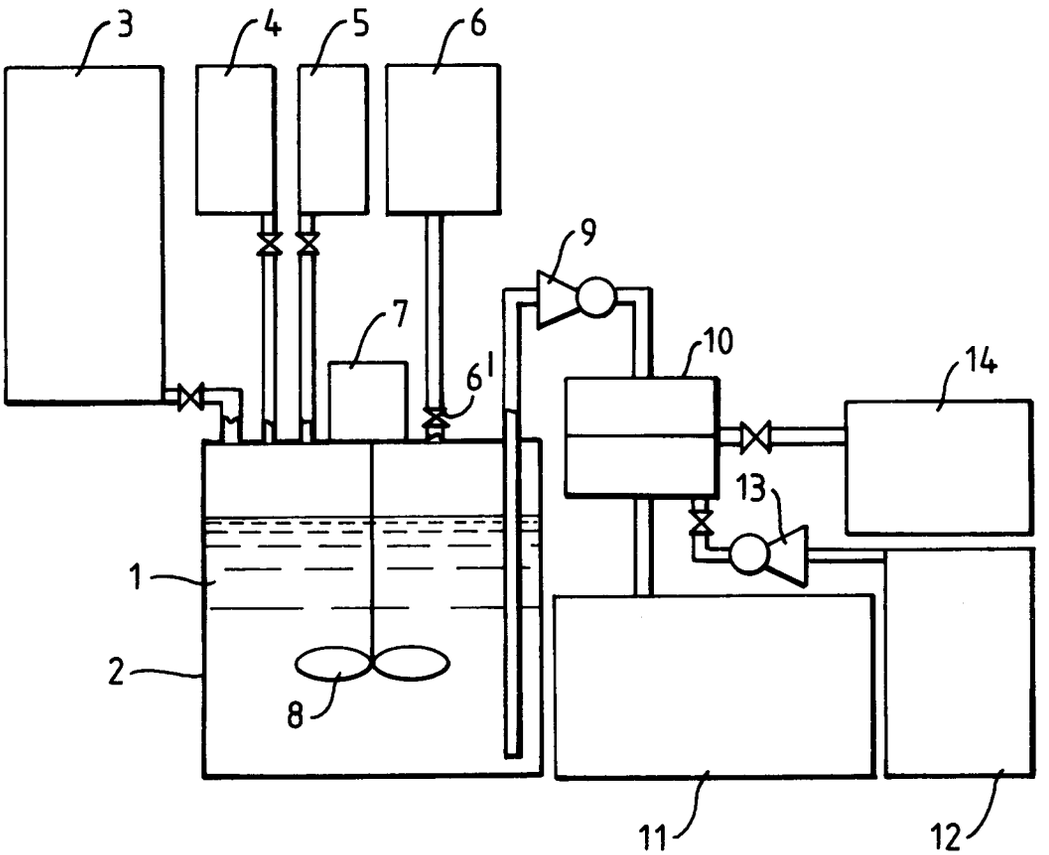

Fig. 4.

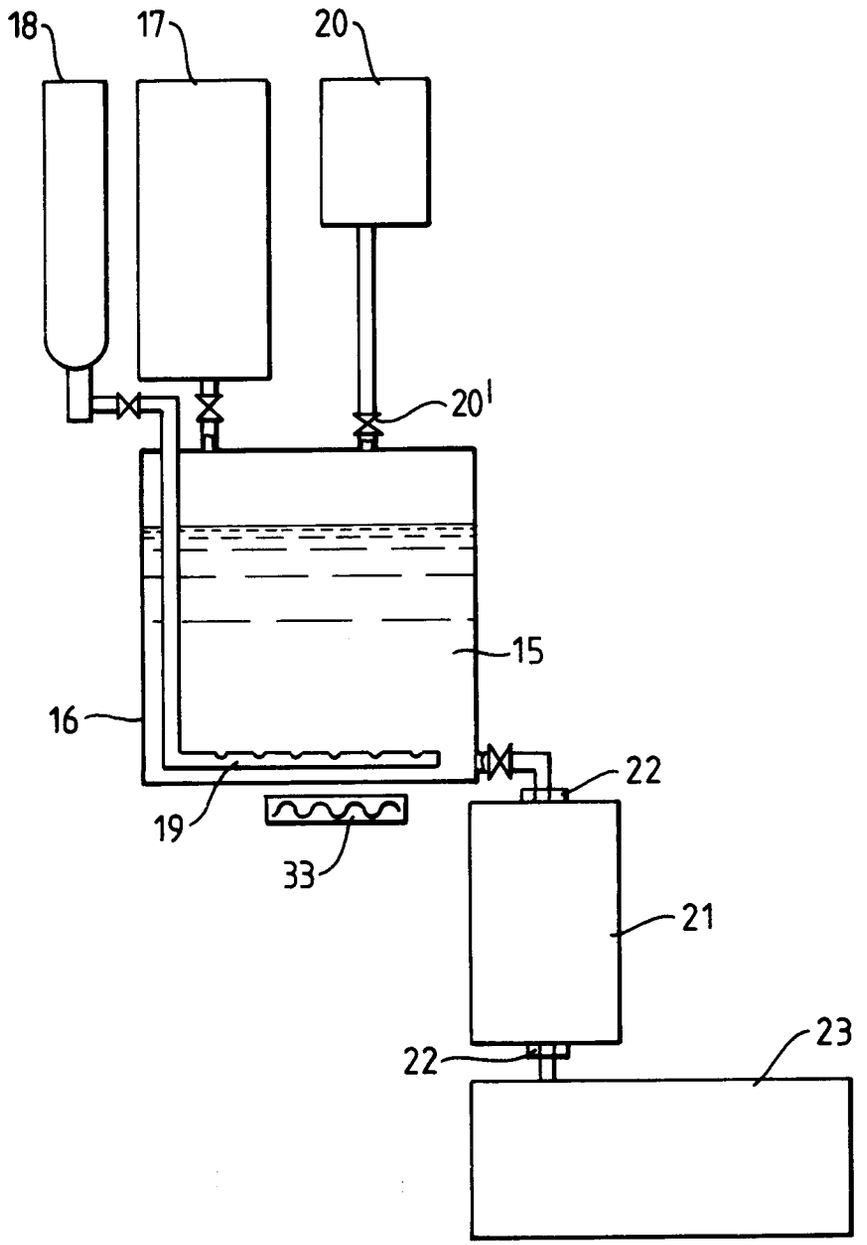
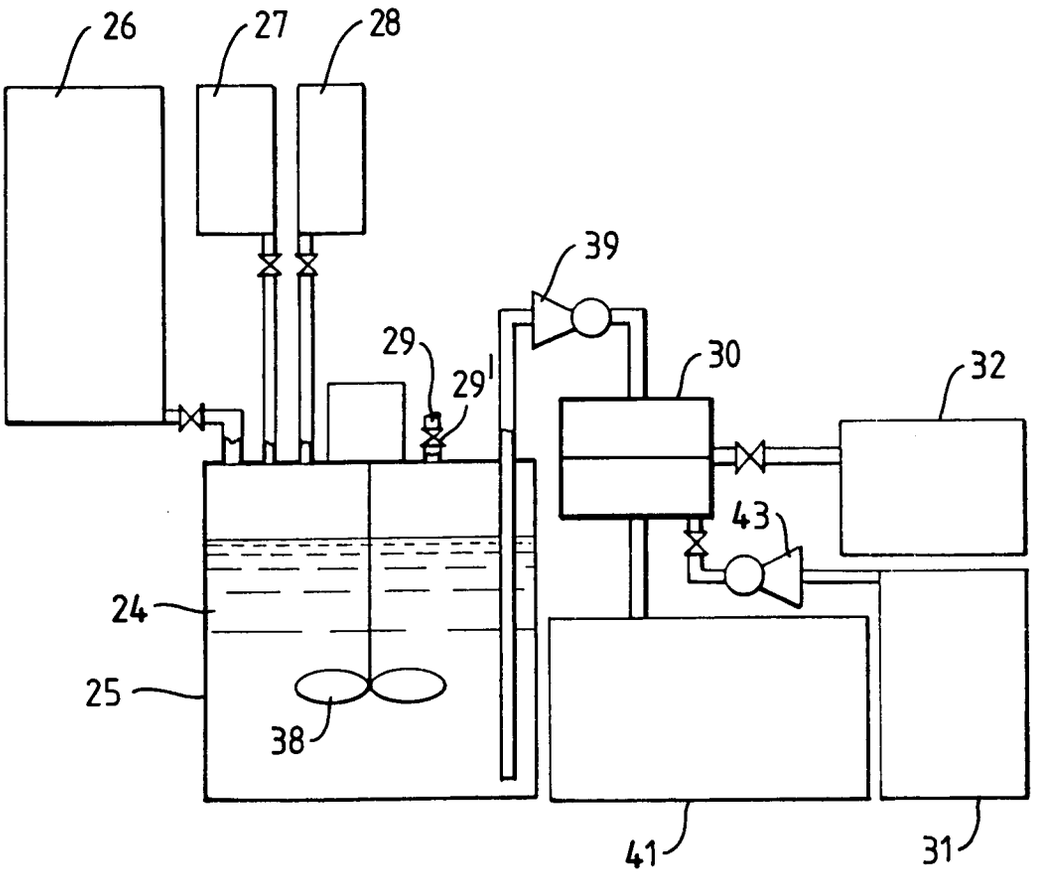
Fig. 5.