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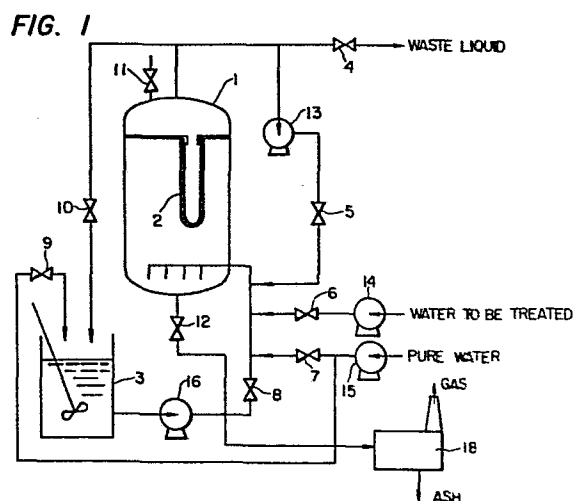
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54 Method for treating a radioactive waste liquid.

57 In a method of removing colloidal substances and suspended solid from waste liquid, oxine-impregnated activated charcoal is employed as an adsorbent in lieu of powdery ion exchange resin. The oxine-impregnated activated charcoal is easily precoated onto filter elements and peeled off after saturated adsorbing capability. The spent adsorbent is dried and incinerated at about 700°C. The volume of radioactive solid waste can be reduced less than 5 % of the original volume of the spent adsorbent by the incineration.



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Method for Treating a Radioactive
Waste Liquid

The present invention relates to a method for treating a radioactive waste liquid which contains colloidal and suspended solid substances.

In the condensation system or in the drain system such as equipment drain or floor drain of nuclear power plants, it is an essential requirement to remove a variety of ions as well as radioactive impurities such as colloidal substances or suspended solids contained in the water, in order to refine and recover the water. Ions dissolved in water can be effectively removed by a conventional column which is filled with a granular anion-exchange resin or a granular cation-exchange resin. The colloidal substances or suspended solids, however, cause the column to be clogged. Therefore, such substances must have been removed beforehand.

Usually the radioactive impurities have been removed by filtration using a demineralizer in which hundreds of filter elements are pre-coated with a mixture of powdery anion-exchange resin and powdery cation-exchange resin such as known "Powdex". (trade name of Graver Water Conditioning Co.). The above system is very effective for refining water, since it captures not only colloidal substances or suspended solids but also captures even anions and cations dissolved therein. This method, however, presents defects

as will be mentioned below.

Namely, the powdery anion-exchange resin and the powdery cation-exchange resin tend to swell or contract when they are subjected to the ion-exchange operation, and further
5 tend to be deformed when they are placed under pressure conditions. Therefore, the filter layer composed of powdery ion-exchange resins becomes gradually densified. The difference in the filtering pressure, therefore, is increased when a flat filter element is used, such as of a stainless-
10 steel gauze. In general, a filter element obtained by winding a nylon yarn or a polypropylene yarn on a hollow metal pipe to a thickness of 10 to 15 mm, or a fibrous ion-exchange resin, has been used. When this type filter element is used, however, troublesome operation is required to wash
15 it in a counter-current manner as compared with the use of stainless-steel gauze. Namely, the filter element accumulates loading and gradually loses its performance. The demineralizer comprising powdery ion-exchange resins therefore must be washed in a counter-current manner more frequently, and the amount of the used radioactive powdery
20 ion-exchange resin is increased.

It is therefore an object of the present invention to provide an improved method of treating radioactive liquid waste which is capable to remove colloidal substances and
25 suspended solids from the waste liquid and also to reduce the amount of the resultant waste solid.

According to the present invention, oxine-impregnated activated charcoal is employed as a pre-coating material in
stead of powdery ion exchange resin for the demineralizer.

30 The invention comprises a method for treating a radioactive waste liquid containing colloidal substances and suspended solids by adsorbing on filter elements precoated with a powdery adsorbent comprising precoating the filter elements

with oxine-impregnated activated charcoal, passing the waste liquid through the filter elements to adsorb the colloidal substances and suspended solids, removing the spent adsorbent from the filter elements and incinerating
5 the removed spent adsorbent in order to reduce the volume of the waste adsorbent.

The oxine-impregnated charcoal is originally developed by the applicant as an adsorption material for radiocobalt ion. The details of the material are described for example
10 in U.S. Patent 4,222,892. By the use of the oxine-impregnated activated charcoal, the final volume of the used precoating material can be greatly reduced to less than 5 % of the original volume, because the used oxine-impregnated charcoal can be easily burned to ash. Also, by the
15 use of the oxine-impregnated activated charcoal, it is possible to eliminate troublesome operations such as regeneration of the ion exchange resin and counter-current washing operations.

Fig. 1 is a system diagram of a processing apparatus according to a preferred embodiment of the present invention;
20 Fig. 2 is a system diagram of an experimental apparatus; Fig. 3 is a characteristic diagram illustrating the relation between the flow rate of water to be treated, the pressure difference and the cobalt concentration in the
25 water to be treated; and Fig. 4 is a characteristic diagram illustrating the relation between the temperature, the weight of the pre-coating material and differential heat.

In the treatment of water or waste water containing radioactive impurities such as colloidal substances and suspended solids from a nuclear furnace of power plant, the
30 powdery activated charcoal having a particle size distribution over a range of 5 to 200 μ m, or the powdery activated charcoal which is impregnated with oxine in an amount

of up to 35 % by the method described in U.S. Patent 4,222,892, or a mixture thereof is dispersed in water, and the dispersion is passed through a filter element to form a filter layer of a thickness of 5 to 15 mm (pre-coating). Water to be treated is then passed through the filter layer, whereby radioactive impurities contained in water are removed and, when oxine is used, ions of cobalt and ions of heavy metals dissolved in water are also removed. In this case, the difference in the filtering pressure is not increased by the deformation which is a serious defect inherent in the use of ion-exchange resin powders. Therefore, a metal gauze made of a stainless steel can simply be used for the filter element. When heavy metals are to be captured by using oxine, the amount of oxine which is eluted is negligibly small even when the water temperature is as high as about 100 °C, provided the amount of oxine does not exceed 10 % with respect to the amount of activated carbon.

When a metal gauze made of a stainless steel is used for the filter element, the filter layer which produces increasing difference in the filtering pressure during the use can be easily and completely peeled off from the filter element by applying a small reverse pressure. The filter layer which is peeled off is dehydrated, dried, and is then gradually incinerated, so that its volume is reduced to less than several percent of its initial volume. In this case, no radioactive substance is emitted, and no harmful gas is generated.

According to the method of the present invention, the filter layer is formed on the surface of the filter element in the following manner. The powdery activated charcoal, the powdery activated charcoal impregnated with

oxine, or a mixture thereof is thrown into water in the pre-coating tank, and is aggitated and dispersed. The dispersion is then passed to the filter element so that it is pre-coated as uniformly as possible. Fine powdery activated charcoal which leaks out first when water is circulated, is also captured by the filter layer. Instead of using activated charcoal impregnated with oxine, the powdery activated charcoal may be dispersed in water beforehand with stirring followed by the addition of a predetermined amount of oxine powder, or the filter element may be pre-coated with the activated charcoal followed by the flow of water in which is dispersed oxine powder. In any case, oxine is strongly adsorbed by the activated charcoal, and ions of heavy metals such as of cobalt are removed in the same manner as by the use of oxine-adhered activated charcoal. The filter element used in the method of the present invention can be other than the one which is usually used for the pre-coated filtration. According to the present invention, a filter cylinder or a filter plate made of a stainless-steel gauze is preferable since it permits the used filter layer to be easily peeled off by applying a reverse pressure and since it is less loaded or less deteriorated by the radiation. Further, the size of the mesh should be 40 to 50 μm .

The effects of the invention will be illustrated below by way of embodiments.

Fig. 1 illustrates the principle of an apparatus of the present invention for removing by filtration colloidal substances and suspended solids from the cooling water or radioactive waste liquid in a nuclear power plant. A cylindrical filter element 2 made of many pieces of stainless-steel metal gauze (having a mesh size of

44 $\pm$ 5 μ m) is installed in a filtering tank 1. A purge valve 11 is opened, and pure water is filled in the tank 1 through a pump 15 and a valve 7. Thereafter, the valves 11, 7 are closed, and the pump 15 is stopped to stop the supply of pure water. On the other hand, a predetermined amount of pure water is introduced into a pre-coating tank 3, and powdery activated charcoal or oxine-impregnated powdery activated charcoal which is a pre-coating material is added in a predetermined amount (1 to 4 kg per square meter of the filtering area) followed by stirring so that it is dispersed in pure water. Valves 8, 10 are then opened, a pump 16 is actuated, and pure water in which is dispersed the pre-coating substance is introduced into the filtering tank 1 and is circulated therein. Valves 4, 5, 6 and 7 are closed. The pre-coating material is permitted to precipitate on the outer surface of the filter element 2, thereby to form a filter layer. Thereafter, the pump 16 is stopped, and the valves 8 and 10 are closed. Then, the valves 4 and 6 are opened, a pump 14 is driven, and water to be treated (such as cooling water or radioactive waste liquid of nuclear reactors) is supplied into the filtering tank 1. Water to be treated is filtered through the filter layer (layer of powdery activated carbon). Further, a pump 13 and a valve 5 are provided to constitute a pressurizing system in order to prevent the filter layer from being peeled off when the pumps 14 and 16 are not working. The operation is discontinued when the colloidal substances or suspended solids in the water to be treated precipitated on the pre-coating material of the filter layer cause the difference in the filtering pressure to be increased (usually, up to about 2 kg/cm²), and compressed water or compressed water admixed with the compressed air is fed through the valve 11, in order to peel off the pre-coating material applied onto the outer surface of the filter element 2. The pre-coating material

which is peeled off is drained out of the filtering tank 1 through a valve 12. Solid portion of the slurry which chiefly consists of the drained powdery activated carbon is separated by the sedimentation method and the
5 filtering method, dried, and is incinerated in an incineration furnace 18 at between 400 to 800 °C. The incineration can be easily controlled by adjusting the blow rate of the air. Waste ash which remains after the incineration includes iron and stable metal oxides. The
10 volume of the solid portion of the waste can therefore be reduced to less than several percent of the initial volume though it may vary depending upon the amount of solid matter that is filtered.

The fundamental requirements and results of the present
15 invention will be mentioned below.

Fig. 2 shows a small filtering apparatus used for studying the fundamental requirements of the present invention. A filter 20 consists of a tube 21 made of acrylic resin (having an inner diameter of 36 mm) and a plug made of
20 polytetrafluoroethylene, and has in the bottom portion thereof a metal gauze 29 (mesh size, $44 \pm 5 \mu\text{m}$) made of a stainless steel which is fixed by packing. Powdery activated charcoal or oxine-impregnated powdery activated charcoal dispersed in water in a pre-coating tank 23
25 using a magnetic stirrer, is introduced into the filter 20 by a pump 25, in order to form a filter layer 30 composed of activated charcoal or oxine-impregnated activated charcoal on the metal gauze. Then, sample water in a sample-water tank 22 is fed into the filter 20 at a constant flow
30 rate using the pump 25. The pressure difference is measured using pressure gauges 26 and 27. Reference numeral 24 denotes a pure-water tank and 28 denotes a flow meter. The experiment is carried out by using fine powdery iron oxide

(Fe_2O_3 , particle diameter 0.5 to 5 μm , average particle diameter 3 μm) as suspended solid substance and cobalt ions (cobalt nitrate whose pH is always maintained at 7.0 ± 0.2 using diluted ammonia water) as dissolved ions.

5 Iron oxide in drained water is measured based upon the oxine-extraction absorptiometric method by separating the sample water by a millipore filter (0.45 micron) and dissolving it in hydrochloric acid, and cobalt is measured

10 by the α -nitroso- β -naphthol-extraction absorptiometric method (quantitative sensitivity, 0.002 ppm).

Experimental results are exemplified below.

Water to be treated:	containing 10 ppm of iron oxide and 1 ppm of cobalt ions.	
Pre-coating material:	3.3 g of powdery activated charcoal impregnated with 10 % of oxine.	
Distribution of particle sizes:	100 - 150 μm	50 %
	50 - 100 μm	30 %
	50 - 10 μm	20 %
Thickness of filter layer:	about 10 mm	
Flow rate:	about 140 ml/min. (about 8 m^3/h)	

Referring to fig. 3, curve A represents the measured data of the filtering pressure which rises relative to the amount of water which has passed through the filter layer when water to be treated is permitted to flow at the above-mentioned constant rate, and curve B represents the amount of cobalt leaked into the drained water. When activated carbon powder (3 g) without oxine is used, the filtering pressure changes almost in the same manner as represented by curve A. Cobalt, however, leaks into the

drained water from the beginning as indicated by a curve C.

In the case of cooling water such as condensed water (which is obtained by condensing the steam in a main condenser) in a practical boiling water nuclear power plant, suspended
5 solid substances composed chiefly of iron oxide called clad are present in water in amounts of about one-thousandth as compared with the amount of iron oxide employed in this experiment. In practice, furthermore, the concentration of
10 cobalt ions is about one-millionth compared with the cobalt ion concentration employed in this experiment. If a demineralizer comprising a stainless-steel gauze pre-coated with the aforementioned powdery activated carbon (or oxine-impregnated powdery activated carbon) is used for the condensation system in the boiling water nuclear power plant, the
15 condensed water in an amount of more than 40 000 tons can be treated per square meter of the filtering area before the filtering pressure difference reaches 2 kg/cm^2 , as is obvious from the above-mentioned experimental results. The spent powdery activated carbon can be removed from the
20 stainless-steel gauze by washing it in a counter-current manner.

The spent powdery activated carbon can be easily burned in the air. No contaminated gas is produced even when the oxine-impregnated activated carbon is burned. These facts
25 are obvious from the results of thermal analysis Fig. 4, in which solid lines represent characteristics of the powdery activated charcoal, broken lines represent characteristics of the oxine-impregnated powdery activated charcoal, and one-dot chain lines represent characteristics of the oxine-impregnated powdery activated
30 charcoal admixed with iron oxide (Fe_2O_3) in a mixing ratio of 1 to 1. The activated charcoal and oxine-impregnated activated charcoal exhibit nearly the same weight and same differential thermal analytic curves. In the case

of the oxine-impregnated activated carbon, a small amount of gas is emitted at about 345 °C presumably due to the decomposition of oxine and the weight is reduced. In practice, however, there is no problem. Both the activated charcoal
5 and oxine-impregnated activated charcoal burns mostly at about 600 °C. When iron oxide is admixed, furthermore, the oxine-impregnated activated charcoal burns quickly at a temperature which is lower by about 100 °C than the above-mentioned temperature even under the same conditions. This
10 is probably because iron oxide serves as a catalyst for the combustion of activated carbon. Experiment further teaches that when the oxine impregnated activated charcoal on which radioactive cobalt is adsorbed is burned, cobalt migrates into the gas in an amount of smaller than
15 one thousandth. As above mentioned, the used activated charcoal or oxine-impregnated activated charcoal can be easily and safely incinerated to greatly reduce its volume.

The present invention presents no problem even when fibers
20 of cotton or paper are added to the powdery activated charcoal.

According to the present invention, the radioactive waste liquids can be effectively refined, and the amount of radioactive wastes can be strikingly reduced.

What is claimed is:

1. Method for treating a radioactive waste liquid containing colloidal substances and suspended solids by adsorbing on filter elements precoated with a powdery
5 adsorbent comprising:
precoating the filter elements with oxine-impregnated activated charcoal,
passing the waste liquid through the filter elements to adsorb the colloidal substances and suspended solids,
10 removing the spent adsorbent from the filter elements and
incinerating the removed spent adsorbent in order to reduce the volume of the waste adsorbent.
2. Method according to claim 1, wherein the activated
15 charcoal is impregnated with oxine prior to the step of precoating.
3. Method according to claim 1, wherein the activated charcoal is impregnated with oxine after it has been precoated on the filter elements.
- 20 4. Method according to any of claims 1 to 3, wherein the removed adsorbent is incinerated gradually at a temperature between 400 °C to 800 °C.
5. Method according to any of claims 1 to 4, wherein the adsorbent is precoated on the filter elements by subjecting fluid
25 pressure against the filter elements and removed by subjecting the filter elements to reverse pressure.

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FIG. 1

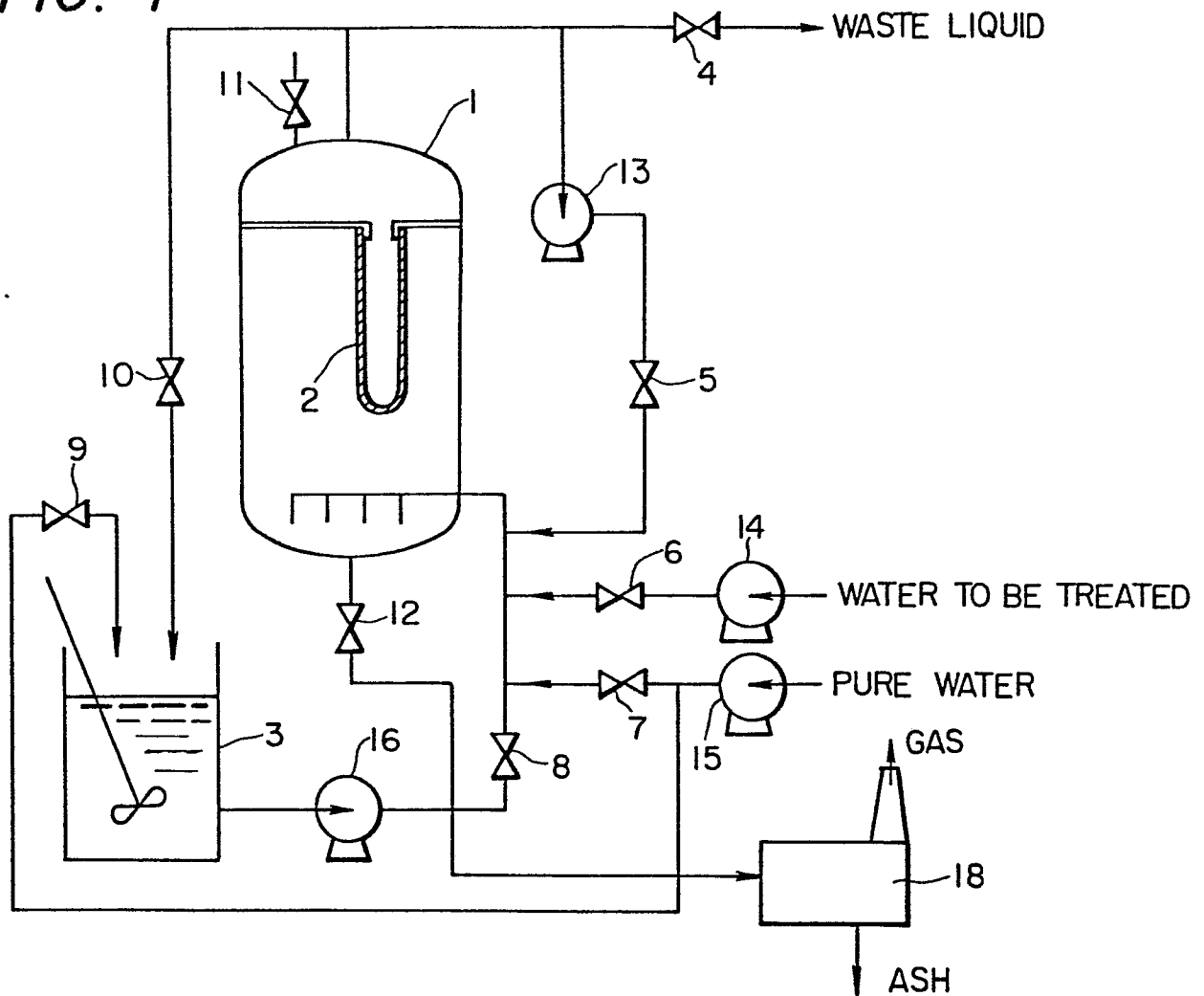
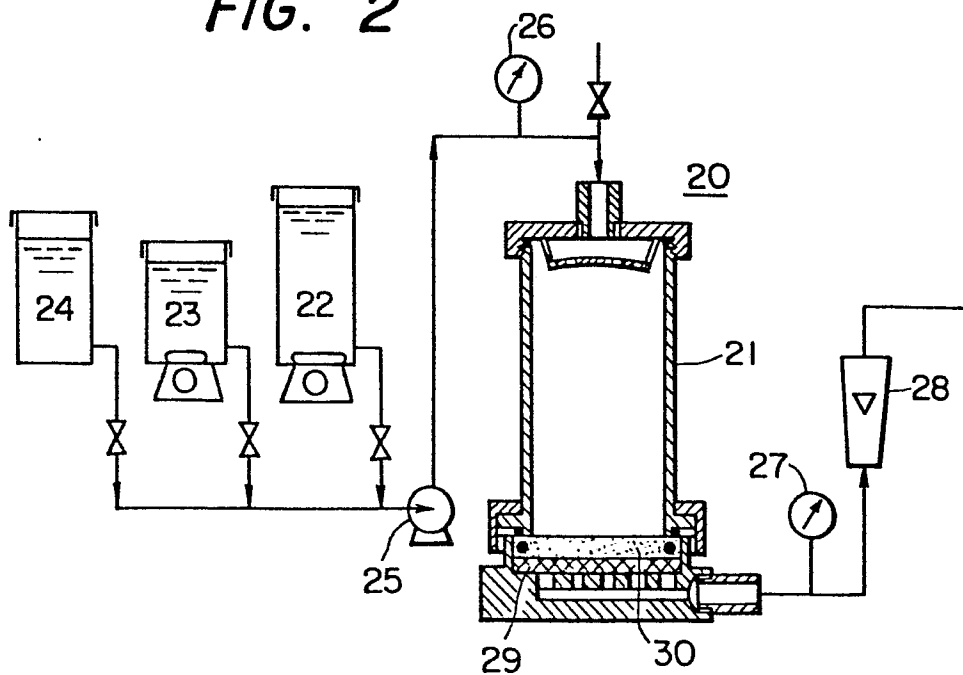


FIG. 2



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FIG. 3

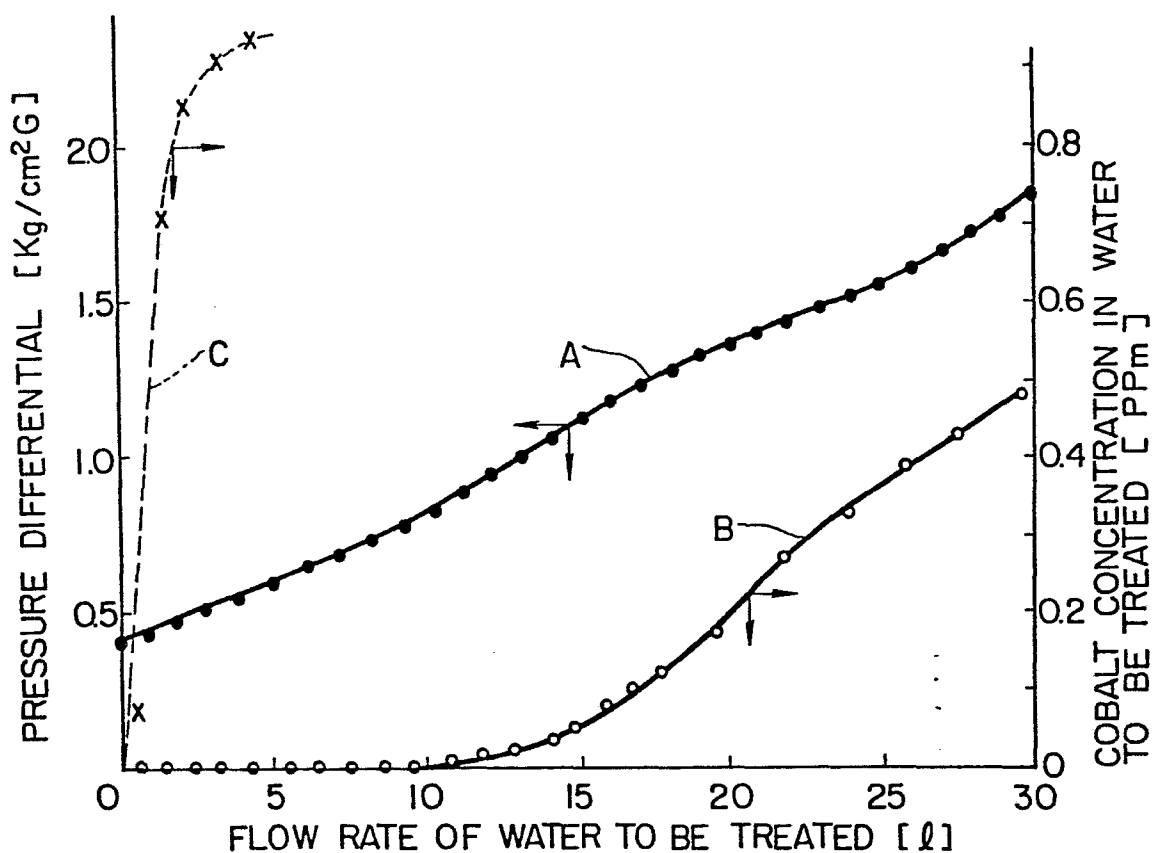


FIG. 4

