

May 16, 1967

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3,320,175

PROCESSING OF RADIOACTIVE LIQUIDS

Filed July 5, 1961

2 Sheets-Sheet 1

FIG.3.

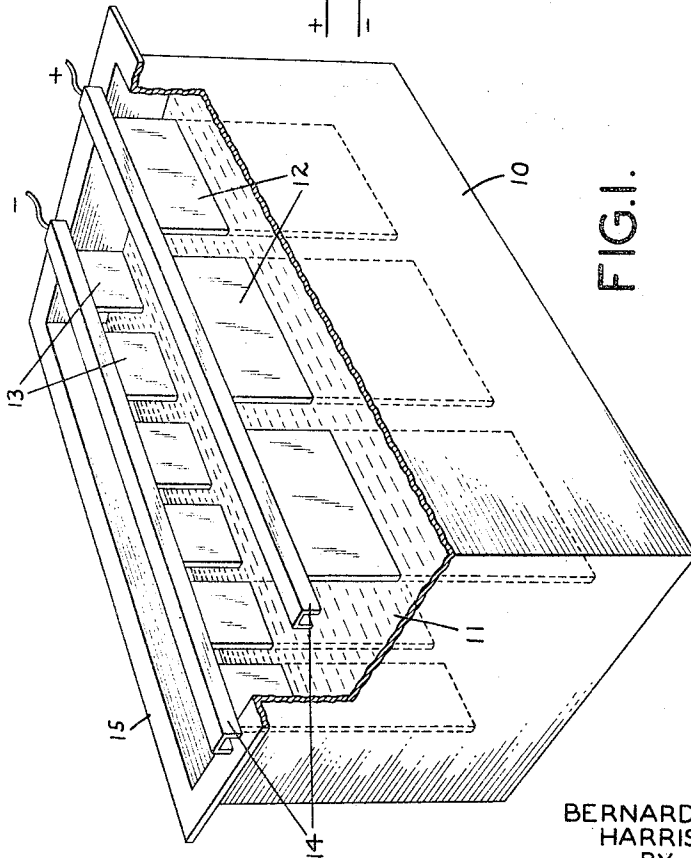
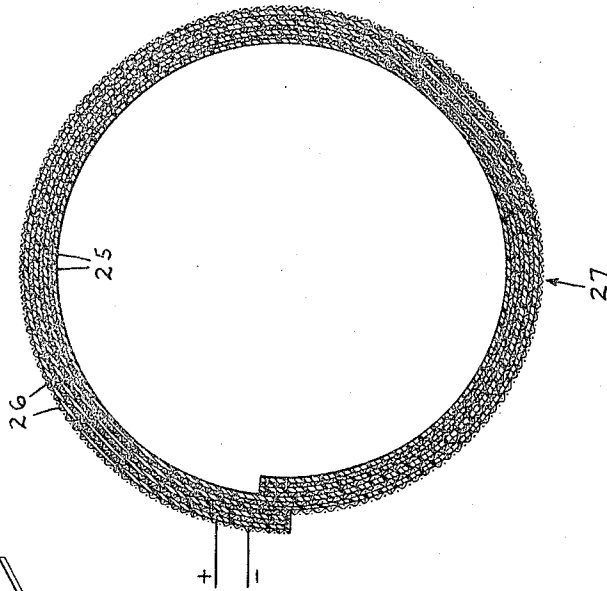


FIG.1.

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2 Sheets-Sheet 2

FIG.4.

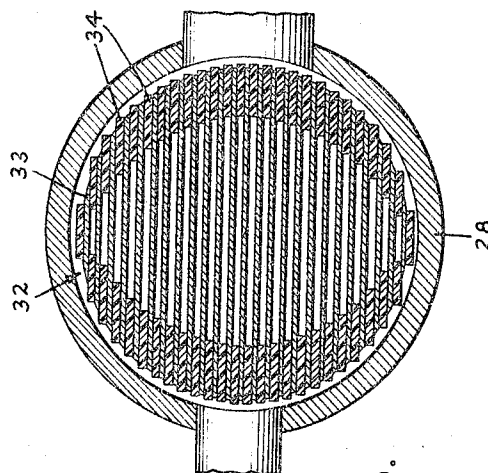
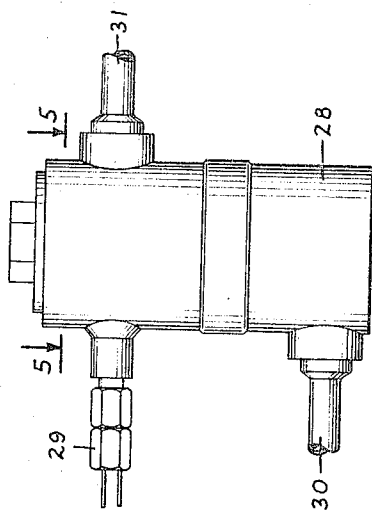
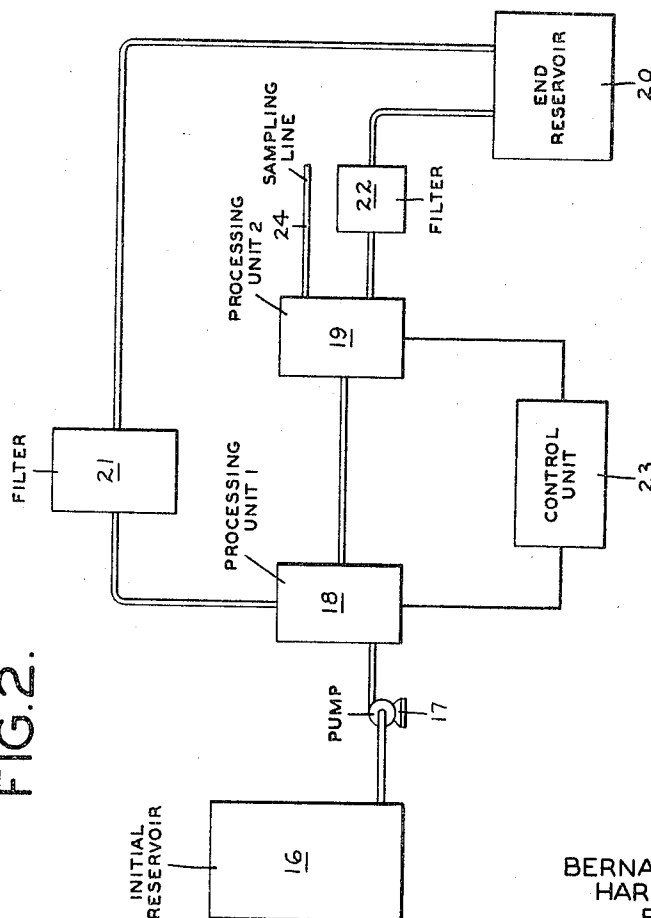


FIG.5.

FIG.2.



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PROCESSING OF RADIOACTIVE LIQUIDS

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3 Claims. (Cl. 252-301.1)

This invention relates to the processing of radioactive liquid wastes and more particularly, to a method and apparatus for the removal of radioactive ions from a liquid.

One of the most important problems in the field of nuclear technology is the processing of liquid wastes containing radioactive isotopes of iron, cobalt, chromium, tantalum, sulphur and other metallic and non-metallic elements. The methods currently in operation to process liquid wastes involve at least one of the following techniques:

- | | |
|----------------------|--------------------|
| (a) evaporation | (d) fixation |
| (b) crystallization | (e) centrifugation |
| (c) demineralization | |

These methods suffer from the disadvantage that the highly radioactive residues remaining after processing are in a form which is difficult for handling and storage. Furthermore, the methods are costly since they utilize relatively expensive material and equipment.

Demineralization with ion exchange resins is somewhat limited in its application to radioactive liquid wastes since the regeneration of the exhausted resin produces highly radioactive liquids which themselves must be processed or stored in shielded tanks. In addition, replacement of the resin involves elaborate and expensive packaging of the exhausted resin for burial. Still another advantage in using ion exchange resin for processing radioactive liquid wastes is the direct effects of radiation on the resin resulting in a decrease in the exchange capacity and degradation of the physical and chemical characteristics of the resin.

Thus, a demand exists in the nuclear industry for a more efficient and economical method of removing radioactive ions from liquid wastes.

It is an object of this invention to provide an economical and efficient method for decontaminating batch quantities or flowing streams of radioactive liquid wastes.

It is another object to provide a novel means for placing certain radioactive isotopes in a form for use as radiation sources.

A further object of this invention is to provide means for removing radioactive ions from a liquid and placing them in a convenient form for handling and storage.

Still another object is to provide a means for augmenting demineralization of radioactive liquid wastes and increasing the operating life of ion exchange demineralizers.

These and other objects and advantages are realized by the application of an electric field to liquid wastes containing radioactive ions to remove the ions from the solution.

This invention may be better understood from the following detailed description taken in conjunction with the accompanying drawings in which:

FIG. 1 is a perspective view of a unit for processing a batch of radioactive liquid wastes;

FIG. 2 is a diagrammatic sketch of a system for processing a continuous flow of radioactive liquid waste materials;

FIG. 3 represents an end view of an electrode found suitable for use in either a batch or flow-type processing unit of this invention;

FIG. 4 is a side view of the housing designed for use with a flow-type processing unit of this invention; and

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FIG. 5 is a view of a section taken on a plane represented by the line 5-5 of FIG. 4 looking in the direction of the arrows.

An illustrative embodiment of the present invention includes a container with electrodes to provide a potential gradient therebetween. When a solution containing radioactive ions is brought into contact with the electrodes, the radioactive metallic ions present are deposited on the electrodes and thus efficiently and quickly removed from the solution.

One embodiment of this invention involves the use of "sacrificial" anodes which go into solution during the period in which a potential is applied across the electrodes. This feature provides additional ions in the solution to replace the radioactive metallic ions being removed and enables the process to proceed at a more efficient rate.

A further advantage in the use of sacrificial anodes lies in the removal of non-metallic radioactive isotopes from liquid wastes by combination of the non-metallic radioactive ions with the ions of the sacrificial anodes to form an insoluble precipitate. An example of this particular embodiment is the removal of radioactive sulphur in the form of a copper sulfate precipitate when the solubility product of the latter is exceeded.

The use of properly designed sacrificial anodes will not reduce the operating life of the processing unit. By preliminary testing and evaluation, anodes can be properly sized in thickness to operate efficiently in a processing unit for lengthy periods before being exhausted.

In the processing of liquids containing radioactive cobalt, there is a tendency toward the formation of insoluble cobaltic hydroxide by virtue of the oxidation of cobaltous ion to cobaltic ion, and subsequent combination with hydroxyl ion present in the liquid. This formation of a precipitate supplements the removal of cobalt by deposition on the cathode and serves to increase the efficiency of the method. Other radioactive ions which form insoluble precipitates in a manner similar to that of cobalt may likewise be removed from waste liquids.

The present invention may be made to operate even more efficiently in many instances by the addition of certain chemicals to the liquid being processed. The use of such additives to control conditions such as pH and ion concentration forms an important subsidiary feature of the invention. Thus, the addition of a chemical which supplies non-radioactive ions of the radioactive isotope being removed will increase the rate of deposition and permit more rapid removal of a greater percentage of the radioactive ions.

A very important advantage of the invention is its adaptation to a continuous or batch operation. A flowing stream or a single batch of radioactive waste can be quickly and efficiently decontaminated by the present method. FIG. 1 shows apparatus suitable for processing a batch of waste material, which includes a container 10, adapted to hold a liquid 11 to be processed. The anodes 12 are made of inert material such as carbon and cathodes 13 are in the form of conductive metal plates. The anodes 12 and cathodes 13 are suspended from metal bars 14 attached to the rim 15 of the container 10. In the particular embodiment depicted in FIG. 1, two cathodes 13 are positioned directly opposite each anode 12.

In FIG. 2 there is depicted a system which has been efficiently used in processing a continuous flow of material. The initial reservoir 16 contains the liquid waste to be processed. The pump 17 pumps the liquid through processing units 18 and 19 connected in series for greater efficiency and then ultimately to the final reservoir 20. The filters shown at 21 and 22 act to remove precipitates formed during the processing. In this embodiment the control unit 23 for the operation is removed from the immediate vicinity of the actual processing equipment to

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eliminate radiation danger to operating personnel. If desired, the liquid may be recycled by returning it to the initial reservoir from the final reservoir and the process repeated. The sampling line 24 permits removal of portions of the processed liquid for determination of the radioactive isotope content.

Processing units may be connected in series for greater operating efficiency. Furthermore, the control unit for operating the continuous system does not require radiation shielding to protect operating personnel, since the control unit can be separated from the processing unit or units, as shown in FIG. 2. The most efficient use of the method of the invention requires testing a sample of the liquid waste initially to determine optimum operating conditions and selection of proper electrode material.

The present invention not only provides an economical and efficient means for decontaminating radioactive liquid wastes, but the compact form of the deposited radioactive material facilitates handling and storage of the material. Since the radioactive isotopes are concentrated within a relatively small area, the protective shielding normally required can be substantially reduced. Furthermore, the processing equipment is not subjected to degradation by the effects of radiation to the extent noted in other processing operations such as where ion exchange resins have been utilized.

Another important advantage of the invention is the fact that under certain easily-determined operating conditions, the radioactive material is in the form of fine-grained adherent deposits which can be utilized as a source of radiation. Thus, the radioactive isotopes are recovered from liquid wastes and made to serve a useful purpose. Other operating conditions will result in the production of non-adherent deposits of radioactive material which are swept away from the electrode and trapped in a filter thus extending the operating life of the unit.

It should be realized that instead of replacing a demineralized with the processing unit of this invention, the operating life of the ion exchange resin can be extended by positioning a processing unit of this invention in front of the resin in the purification loop. In this manner, the unit will supplement the resin by electro-deposition of ions which ordinarily occupy ion exchange resin sites in the demineralizer.

The design of the electrode is important if optimum operating conditions are to be attained. FIG. 3 shows a "wrap-around" type electrode consisting of alternate layers of fiberglass insulation 25 and brass sheeting 26 rolled into a cylinder 27 to fit the particular housing of the processing unit. This design offers a large electrode surface area with relatively close spacing.

FIG. 4 shows the construction of a container designed to house either a "wrap-around" or "cell-type" electrode in a continuous operation. The container 28 is preferably constructed from a sturdy material such as cast iron. The electrical connections are made with the aid of an insulated electrical penetration fitting 29. The waste material enters the housing through the inflow conduit 30 and is removed by way of the outflow conduit 31 after coming into contact with the electrodes contained within housing 28.

A "cell-type" electrode in cross-section is shown in FIG. 5. The electrode 32 allows close electrode spacing and presents a large electrode area per unit volume of liquid passing through the cell. It is constructed of brass plates 33 about 0.032 inch thick, with plastic strips 34 about 1/16 inch thick used as insulators. The electrical connections are such that each alternate electrode is of the same electrical polarity.

If desired, the electrode may be placed within a suitable container (not shown) which is then inserted into the housing structure depicted in FIG. 5. Of course, the inner container would be perforated to enable the radioactive effluent to contact the electrode.

The following examples further illustrate the invention. In these examples, the electrodes were chemically cleaned

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prior to the operation. Cleanliness of the electrodes is an important factor in obtaining good adherent deposits.

Example 1

In this example, a solution containing metallic ions was tested in order to determine the feasibility of quickly and economically removing radioactive ions from solution. Initial tests were run using reactor grade water containing very small concentrations of radioactive cobalt. The concentration of cobalt was too dilute for accurate quantitative determination. By counting the gamma radiation, it was determined that approximately 80% of the Co⁶⁰ in solution was removed in 15 minutes of operation. For convenience, the remaining tests were conducted with non-radioactive ions.

Example 2

The cathodes of the processing unit were various metal plates such as copper while the anodes were inert carbon plates. The electrodes were suspended from copper bars in a tank as shown in FIG. 1. Each carbon anode was positioned directly opposite two metal cathodes with the distance between the anodes and cathodes being approximately three inches.

A batch of solution was prepared containing ions of cobalt and iron and was processed utilizing the batch unit. Both cobalt and iron were deposited from the solution on the cathodes when a current of 400 milliamperes was applied. This mixed ion solution contained the following components:

	G./L.
CoSO ₄ ·7H ₂ O	252
NaCl	7
H ₃ BO ₃	28
FeCl ₂ ·4H ₂ O	120
KCl	90

Example 3

The following solution was processed using a batch type unit as shown in FIG. 1:

Cobaltous sulfate·7H ₂ O	g./l.	2
Sodium chloride	mg./l.	100
Boric acid	mg./l.	200

The boric acid additive acted as a buffering agent. A receptacle was filled with this cobalt solution and a "wrap-around" type electrode constructed as shown in FIG. 3 was introduced into the container. A current of about 300 milliamperes was supplied to the electrodes (1.29 ma./cm.²). After about 30 seconds of operation, the characteristic pink color of the cobalt solution disappeared indicating that a large percentage of the cobalt ions in the solution had been removed. After the electrode was withdrawn, a brownish-colored precipitate was discovered suspended in the treated solution. This suspended precipitate, identified as cobaltic hydroxide, was removed from the treated solution by filtration. The filtered solution was analyzed to determine the amount of cobalt remaining in the solution after processing. The result of the analysis is as follows:

Co Content Before Processing (p.p.m.)	Co Content After Processing (p.p.m.)	Percent Removed
470 1284	25.4 4.0	94.6 98.6

¹ This series of experiments in the second line utilized a double fiberglass screening rather than a single layer as insulation.

The extraordinary efficiency of the method of the present invention is clearly illustrated by this example. A thirty second operation resulted in almost complete removal of the cobalt isotope.

Example 4

In this example, a flow model processing unit as described in FIG. 4 was used to process a continuous stream of material. A five-micron filter was installed in the processing loop downstream from the unit to remove the hydroxide precipitate. Other components in the processing loop included a 4.5 gallon/minute pump, a flowmeter, a twenty-micron pre-filter, the processing unit itself and the necessary control equipment. Initial tests were conducted using a "wrap-around" type electrode installed in the processing unit housing. With both the pre-filter and post-filter in the test loop, the maximum flow rate obtained was one gallon per minute. The unit performed well for several minutes using a current of 800 milliamperes (0.14 ma./cm.²) and a current of 500 milliamperes (0.09 ma./cm.²). After several minutes' operation, however, the unit removal effectiveness decreased. It was noted that the fiberglass screening used as the insulation on the electrode had retained a considerable amount of fluid. The water-filled insulation apparently acted as a physical barrier tending to prevent the migration of the ions to the electrodes and decreasing the electrodeposition process. After the fiberglass insulation had been allowed to dry, the electrode again operated effectively.

Because of the high pressure drops in the system, the five-micron post filter was removed from the loop and replaced with a twenty-micron filter. This larger post filter eliminated the need for a pre-filter. With the five micron filter removed, a two gallons per minute flow rate was realized. A "cell-type" electrode was then substituted for the "wrap-around" electrode. This electrode was positioned in the housing of the unit and the necessary electrical connection made by use of the fitting as shown in FIGURES 4 and 5. The pump was ultimately bypassed to decrease the flow rate even further and provide a gravity feed system. After several minutes of efficient processing under an applied current of 800 milliamperes (0.52 ma./cm.²), a greenish foam developed which proved to be copper sulfate and which was removed by providing a hole in the housing cap. This outlet became the liquid and foam outlet to the filter and the former outlet tube was used as a sampling line. With the system reassembled and the unit operated at 800 milliamperes, a considerable amount of foam and precipitate was observed in the outlet line to the post filter.

The following cobalt solution was processed using this flow model unit:

CoSO ₄ ·7H ₂ O	g./l.	2
NaCl	mg./l.	100
H ₃ BO ₃	mg./l.	200

The results are as follows:

Co content original solution (p.p.m.) 315

First pass (p.p.m.):	Percent removed
90	71.5
Final pass (p.p.m.):	
3	99.1

It can readily be seen that the present invention is extremely versatile in its application to the processing of wastes containing radioactive ions in solution.

While particular embodiments of the present invention are shown and described for purposes of illustration, it is apparent that changes and modification may be made without departing from this invention in its broader aspects. Therefore, the invention described herein is not to be construed as limited to the specific embodiments described, but is intended to encompass all modifications thereof coming within the scope of the following claims.

We claim:

1. A method for processing radioactive liquid wastes which comprises contacting a liquid containing radioactive non-metallic ions with electrodes including at least one anode and one cathode, the anode being fabricated from a metal which is reduced and goes into solution thereby combining with the non-metallic ions to form an insoluble precipitate.

2. A method for processing radioactive liquid wastes containing radioactive cobalt which comprises contacting a liquid waste material containing a radioactive isotope of cobalt with electrodes and simultaneously depositing the cobalt on the cathode and precipitating cobalt in the form of cobaltic hydroxide.

3. A method for processing radioactive liquid wastes containing radioactive sulphur which comprises contacting a liquid waste material containing a radioactive isotope of sulphur with electrodes including at least one anode and one cathode, the anode containing copper, thereby precipitating sulphur in the form of copper sulfate.

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