

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number:

0 244 922
A1

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 87300067.3

(51) Int. Cl. 4: **G21F 9/12**

(22) Date of filing: 06.01.87

(30) Priority: 08.05.86 US 860922

(43) Date of publication of application:
11.11.87 Bulletin 87/46(84) Designated Contracting States:
DE ES FR GB IT SE(71) Applicant: **WESTINGHOUSE ELECTRIC
CORPORATION**
Westinghouse Building Gateway Center
Pittsburgh Pennsylvania 15222(US)(72) Inventor: **Saha, Anuj Kumar**
4878 Winterway
Hamburg New York 14075(US)(74) Representative: **van Berlyn, Ronald Gilbert**
23, Centre Heights
London, NW3 6JG(GB)(54) **Apparatus and method for removing strontium ions from aqueous solutions.**

(57) Apparatus for removing strontium ions from an aqueous solution having a pH of about 7, and possibly containing solid particulate matter. The apparatus comprises a container, particulate zeolite at least partially filling the container, means for continuously admitting the aqueous solution to the container to the top of the zeolite, a microporous filter within the zeolite under the aqueous solution in the container, and means for drawing the aqueous solution through the microporous filter and out of the container. Also a method of removing strontium ions from an aqueous solution containing solid particles by adjusting the pH of the aqueous solution to from 6.5 to 7.5, prewashing zeolite with a solution of a sodium salt, and drawing the aqueous solution through the prewashed zeolite, then through a microporous filter.

EP 0 244 922 A1

APPARATUS AND METHOD FOR REMOVING STRONTIUM IONS FROM AQUEOUS SOLUTIONS

This invention relates to an apparatus and method for removing strontium ions from aqueous solutions.

One product of water-cooled nuclear reactors and reprocessing plants is large quantities of slightly radioactive-water. This water is stored and processed in large lagoons until its radioactivity can be reduced to a level sufficient to meet discharge requirements for various radioactive isotopes that may be in the water. A radioactive isotope that present particular difficulties is the strontium 90 isotope, which has a discharge limit of 3×10^{-7} microcuries/cc in an uncontrolled area. Efforts to remove the strontium 90 from the water by various means have not proved to be successful. For example, running the water through a weak acid carboxylic cation exchange resin did not remove sufficient strontium 90 ions to meet the discharge requirements. Even a combination of carbon filtration followed by organic ion exchange using a commercial process failed to remove sufficient strontium 90 ions to meet the discharge requirements.

Accordingly, the invention resides in an apparatus for removing strontium ions from an aqueous solution having a pH of about 7, and possibly containing solid matter characterized in that said apparatus comprises a container; particulate zeolite at least partially filling said container; means for continuously admitting said aqueous solution to said container to the top of said zeolite; a microporous filter within said zeolite under said aqueous solution in said container; and means for drawing said aqueous solution through said microporous filter and out of said container.

The invention also includes a method of removing strontium ions from an aqueous solution containing solid particles characterized by adjusting the pH of said aqueous solution to from 6.5 to 7.5; prewashing zeolite with a solution of a sodium salt; and drawing said aqueous solution through said prewashed zeolite, then through a microporous filter.

By a method and apparatus of the present invention strontium 90 can be effectively removed from waste water. This can be accomplished even when the discharge water contains particulate matter which would otherwise plug or foul other types of apparatus. The method and apparatus of this invention employ inexpensive materials in a relatively simple configuration which is easy to operate.

In order that the invention can be more clearly understood, a preferred embodiment thereof will now be described, by way of example, with reference to the accompanying drawing which is a side view, in section, of an apparatus for removing strontium ions from aqueous solutions containing particulate matter.

Referring to the drawing, a large container 1, preferably constructed of carbon steel or high density polyethylene, having sides 2, a lid 3 and a heavier bottom 4, and fitted with three lifting lugs 5 (only one shown), is filled with zeolite 6. Contaminated water containing strontium ions and particulate matter enters tank 1 through pipe 7 where it fills the tank approximately to the level 8 of zeolite 6. The contaminated water moves down through the zeolite and passes into microporous filter tube 9 which is sealed at each end. The water is drawn from the inside of the tube up through pipe 10 by means of pump 11 for discharge or storage. A second tube 12 also extends from the inside of microporous filter tube 9 to the outside of tank 1 for the purpose of removing the last drops of water from the tank prior to its disposal. Tank 1 is also provided with a vent 13 and with two spare nozzles 14 (only one shown for simplicity) for the purpose of sluicing fresh zeolite slurry in and sluicing exhausted zeolite slurry out (if required for any reason).

Water can be treated contaminated by strontium ions, particularly strontium 90, which is radioactive. The water may also contain precipitated compounds or undissolved particular matter. Typically, pond/fuel pool/lagoon water from nuclear power plants may contain from 10 ppm (parts per million) to 1.0% (all percentages herein are by weight) of particulate matter, and from 0.01 ppt (parts per trillion) to 10.0 ppb (parts per billion) strontium, of which from 90% to 99% (based on strontium weight) is strontium 90. The waste water may also contain various other ions that are radioactive, such as cerium, as well as toxic ions such as antimony. The apparatus and process of this invention will remove some or all of these other ions too, provided they are cations. The waste water should contain no organic liquids, as organic liquids tend to plug the zeolite and render it ineffective. In addition, the water being treated must have a pH of about 7, and preferably of from 6.5 to 7.5, because it has been found that strontium removal is very pH sensitive. That is, at a pH of less than about 6, the strontium will not be removed, or will be removed by only a small amount. If the pH of the water is not about 7, it should be adjusted by the addition of a base or an acid, such as sodium hydroxide or hydrochloric acid solution.

Apparatus used in this invention may be constructed of various materials as is known in the art. The microporous tube, for example, can be constructed of stainless steel, polypropylene, fluorocarbons, or other materials. Stainless steel is preferred as it is inexpensive, readily available, and has been found to work well. The microporous filter may be of various shapes, but tubes are preferred as they are the most convenient and available. The pore size in the microporous filter will depend to some extent upon the size

of the particulate matter that is present in the contaminated water that one wishes to remove. A preferred pore size is a nominal size of 1 micron, which means that any particulate matter larger in size than 1 micron will not pass through the microporous filter. Typical tube sizes range from 1 to 5 inches in diameter, from 15 to 60 inches long and from 0.5 mm to 2.0 mm in thickness.

- 5 The zeolite that is placed within the tank is preferably prewashed with an aqueous solution containing a salt of sodium. This is because some zeolites, particularly some clinoptilolites, contain potassium, and potassium-containing zeolites are not as effective as sodium-containing zeolites. Washing the zeolite with a solution of a sodium salt replaces the potassium in the zeolite with sodium and results in a higher decontamination factor because more strontium is removed from the aqueous solution by Na^+ replacement.
- 10 The preferred sodium salt is sodium chloride because it is inexpensive and readily available, but other sodium salts such as sodium nitrites and sodium nitrates can also be used.

Zeolite is a hydrated aluminum silicate which may contain calcium, sodium, or potassium, and has the general formula $\text{Na}_2\text{O} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$, $\text{CaO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$, or $\text{Na}_2\text{O} \cdot \text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 5\text{O}_2 \cdot 5\text{H}_2\text{O}$. Either natural or synthetic zeolites can be used, but natural (or mineral) zeolites are preferred as they are less expensive and equal or more effective. Examples of suitable zeolites include clinoptilolite, chabazite, mordenite, phillipsite, and erionite. Clinoptilolite is preferred as it is the most effective for removing strontium. A suitable particle size for the zeolite is about 20 to about 50 mesh, although other particle size ranges may also be used.

15 In operating the apparatus, the prewashed zeolite is sluiced in the tank with the top leveled, and the contaminated water is admitted until it reaches the top of the zeolite. The pump is then started, which sucks the contaminated water through the zeolite, the microporous filter, and out of the tank. Should the microporous filter become plugged, the pump can be reversed temporarily to force the particulate matter away from the filter and unplug it - a process known as "backflowing." The water discharged from the tank is periodically tested for radioactivity. A rise in the radioactivity of the water being discharged from the tank indicates that the zeolite has become exhausted. The zeolite can then be removed and replaced with fresh zeolite, or the entire tank can be drained of fluid and discarded as radioactive waste.

25 Various zeolites were tested for their capacity to absorb strontium and cesium. The tests were conducted by placing 0.01 gm of the zeolite in a beaker and agitating in a 50 ml 0.5 w/o nitric acid solution for 24 hours. The strontium and cesium loading were measured by a multi-channel analyzer

30 The following table gives the results:

35

40

45

50

55

	Ion Exchange Material	Zeolite Loading, Micro Ci/g		Total
		Sr	Cs	
5	Clinoptilolite*	5.298E+00	2.381E+01	2.911E+01
	Phillipsite*	6.137E+00	3.703E+01	4.317E+01
	Erionite*	6.247E+00	4.511E+01	5.136E+01
	Mordenite*	6.427E+00	2.350E+01	2.993E+01
10	Chabazite*	6.345E+00	4.451E+01	5.086E+01
	"R&H CS-100" (1)	5.624E+00	1.681E+00	7.305E+00
	"Ionsiv A-51" (2)	6.179E+00	5.092E+00	1.127E+01
	"Ionsiv IE-95" (3)	6.432E+00	4.149E+01	4.792E+01
	Chabazite**	6.089E+00	4.430E+01	5.039E+01
15	Clinoptilolite**	6.467E+00	2.231E+01	2.878E+01

* Sold by Tenneco Minerals (formerly Phelps Dodge Zeolites)

** Sold by Teague Mineral Products

(1) CS-100, Duolite resin (weak acid resin) sold by Rohm & Hass under this trade designation.

(2) Linde A-51 Zeolite (prepared zeolite) sold by Union Carbide under this trade designation.

(3) Linde IE-95 Zeolite (prepared zeolite) sold by Union Carbide under this trade designation.

The above table shows that clinoptilolite from Teague Mineral Products had the highest loading for Sr isotopes. This clinoptilolite is mostly a potassium clinoptilolite. It is not even washed with any sodium salts.

Claims

1. Apparatus for removing strontium ions from an aqueous solution having a pH of about 7, and possibly containing solid matter characterized in that said apparatus comprises a container; particulate zeolite at least partially filling said container; means for continuously admitting said aqueous solution to said container to the top of said zeolite; a microporous filter within said zeolite under said aqueous solution in said container; and means for drawing said aqueous solution through said microporous filter and out of said container.

2. Apparatus according to claim 1, characterized in that the zeolite is prewashed with a solution of a sodium salt.

3. Apparatus according to claim 2, characterized in that the sodium salt is sodium chloride.

4. Apparatus according to claim 1, 2 or 3, characterized in that the microporous filter is in the form of a tube.

5. Apparatus according to any of claims 1 to 4, characterized in that the aqueous solution enters the container at the top of said container, and the microporous filter is at the bottom of said container.

6. Apparatus according to any of claims 1 to 5, characterized in that the aqueous solution has a pH of from 6.5 to 7.5.

7. Apparatus according to any of claims 1 to 6, characterized in that the apparatus includes means for backflowing the aqueous solution through the microporous filter.

8. Apparatus according to any of claims 1 to 7, characterized in that the microporous filter is made of stainless steel.

9. Apparatus according to any of claims 1 to 8, characterized in that the microporous filter has a nominal pore size of one micron.

10. Apparatus according to any of claims 1 to 9, characterized in that the zeolite is clinoptilolite.

11. A method of removing strontium ions from an aqueous solution containing solid particles characterized by adjusting the pH of said aqueous solution to from 6.5 to 7.5; prewashing zeolite with a solution of a sodium salt; and drawing said aqueous solution through said prewashed zeolite, then through a microporous filter.

5

10

15

20

25

30

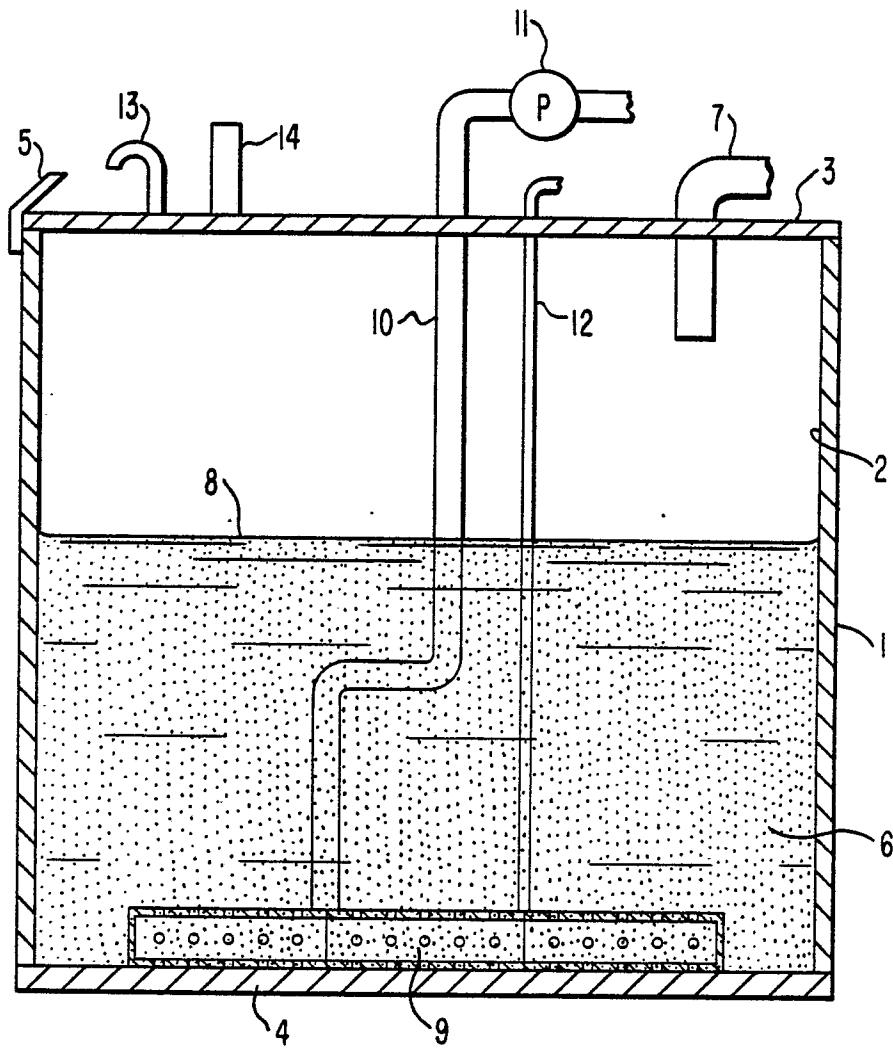
35

40

45

50

55





DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
X	US-A-4 107 044 (LEVENDUSKY) * Claims 1,3 *	1,4,5, 7,11	G 21 F 9/12
Y		1,10	
Y	--- CHEMICAL ABSTRACTS, vol. 76, no. 18, 1st May 1972, page 270, abstract no. 103511r, Columbus, Ohio, US; L. ADAM et al.: "Removal of radioactive pollutants form water, using mineral substances of natural domestic origin", & BANYASZ. KUT. INTEZ., KOZLEM. 1971, 15(2), 89-96	1,10	
A	--- US-A-3 747 768 (BARRERA) -----		TECHNICAL FIELDS SEARCHED (Int. Cl.4) G 21 F C 02 F C 22 B
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 13-08-1987	Examiner NICOLAS H.J.F.
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			