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(54) Method of removing transition metals from complexing agent-containing solutions.

(57) Method of removing transition metals from a decontamination solution containing a complexing agent having an equilibrium constant for the ferric ion complex formation reaction of greater than 10^{22}, such as ethylene diamine tetraacetic acid. An anion exchange resin is loaded with the complexing agent or one of its salts, and the solution is passed through the anion exchange resin. The method is applied to decontamination solutions which are used to clean cooling systems of nuclear reactors.

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METHOD OF REMOVING TRANSITION METALS FROM COMPLEXING AGENT-CONTAINING SOLUTIONS

This invention relates to a method of removing transition metals from complexing agent-containing solutions.

Deposits which contain radioactive elements often form in the cooling systems of nuclear reactors. In order to safely maintain and repair the cooling system, it is necessary to remove these radioactive deposits. This can be accomplished, for example, by using an oxidizing solution of alkali permanganate followed by a decontamination solution of oxalic acid, citric acid, and ethylenediamine tetraacetic acid (EDTA). The EDTA forms a complex with the radioactive metal ions in the deposits, which solubilizes them. The decontamination solution is circulated between the cooling system and a cation exchange resin which exchanges the metal ions on the resin and frees the EDTA to solubilize additional metal ions.

A major difficulty with this process, however, is that EDTA does not readily yield up metal ions, particularly the ferric ion, to the cation exchange resin. Thus, the concentration of the metal ion-EDTA complex builds up in the decontamination solution until it is no longer effective in solubilizing the metal ions in the deposits. When this happens, it is necessary to add fresh EDTA to the solution. This means that the solution must be constantly monitored to determine if the EDTA has been depleted so that more can be added. Also, great care must be taken not to add excess EDTA since EDTA is not very soluble unless it has formed a complex with metal ions, and precipitated EDTA can itself be difficult to remove from the cooling system. Moreover, if excess EDTA is added, not only is the reagent wasted, but the additional EDTA must be removed from the solution at a later stage which adds to the volume of radioactive waste.

Accordingly, the present invention resides in a method of removing transition metals from a solution containing a complexing agent having an equilibrium constant for the ferric ion complex formation reaction of at least 10^{22}, characterized by loading an anion exchange resin with said complexing agent or a salt thereof and circulating said solution through said anion exchange resin.

Preferably, the complexing agent is ethylene diamine tetraacetic acid or an alkali metal salt thereof.

We have discovered a process for removing transition metal ions from a decontamination solution containing a selected complexing agent while regenerating that agent. Unlike the prior process which used a cation exchange resin, our process uses an anion exchange resin. The anion exchange resin is preloaded with, say, EDTA anion so that the entire metal ion-EDTA complex deposits on the ion exchange resin, releasing fresh EDTA from the anion exchange resin into the solution. Thus, the concentration of uncomplexed EDTA in the solution remains fairly constant and it is not necessary to monitor the solution for the EDTA concentration or to add fresh EDTA.

The process of this invention can thus be applied to any solution containing a complex of a transition metal with a complexing agent having an equilibrium constant for the ferric ion complex formation reaction of greater than 10^{22}. Examples of such complexing agents include ethylenediaminetetraacetic acid (EDTA), trans, 1, 2 diaminocyclohexanetetraacetic acid (DCTA), and oxybis (ethylenediaminetetraacetic acid). Common transition metals found in nuclear reactor decontamination solutions include iron, cobalt, nickel, and chromium. The temperature of the solution should be at least 40°C in order to keep this complexing agent in solution and prevent it from precipitating. The temperature of the solution should be below about 100°C, however, as anion exchange resins and the reagents used in the solution may decompose above that temperature. The pH of the solution is not critical but it is typically from 2 to 2½ for most decontamination solutions due to the acidity of reagents which are present.

In the first step of the process of this invention, therefore, an anion exchange resin may be loaded with EDTA. Any anion exchange resin is suitable and may be used in this invention. The resin should be loaded with only EDTA and not with any other additional complexing agents because as the metal EDTA complex is absorbed by the resin, another anion (i.e., nitrilo triacetic acid NTA, citric, or oxalic) would be released, diluting the concentration of EDTA in the solution. Other complexing agents, such as NTA, or organic acids, such as citric acid and oxalic acid form much weaker transition metal complexes compared to those formed with EDTA, and metals complexed with these other agents can be removed from solution by cation exchanges. This is not the case for EDTA-metal complexes, and as a result, the metal remains in solution using conventional removal methods.

The anion exchange resin is most conveniently loaded with the EDTA anion by preparing a solution of the EDTA and passing the solution through the anion exchange resin. It is desirable to use a solution of an EDTA salt, preferably an alkali earth metal salt, such as sodium EDTA, to load the anion exchange resin with the EDTA anion as this releases sodium hydroxide rather than just water into the solution. Since NaOH is highly alkaline, (pH~12-14) the pH of the solution exiting the column, after an initial rise, will fall back down to the pH of the sodium EDTA (pH~4-5) as fewer hydroxide groups of the preferred strong base anion exchange resin are replaced by the EDTA anion. Thus, by monitoring the pH of the solution leaving the resin, one can then determine when the resin has been fully loaded. After the pH falls to below about 6, the resin should be considered to be fully loaded with EDTA anion. While the acid form of EDTA can be used, it is more difficult to determine when the resin has been loaded because without the presence of the sodium ion, the solution leaving the columns will be at approximately a neutral pH value (~7). Thus, the difference in pH values of the column feed (about 4.5) and the column effluent (about 7) is significantly less than when the sodium salt is used. Also, the acid form of EDTA is not very soluble in water which means that the solution must be more dilute.

In the next step of the process of this invention, the decontamination solution containing the metal ion-EDTA complex is circulated between the EDTA-loaded anion exchange resin and the reactor cooling system, or the portion thereof that is being decontaminated, such as the steam generator of a pressurized water reactor or a boiling water reactor. As the metal ion-EDTA complex is absorbed onto the EDTA anion exchange resin, fresh EDTA is released into the decontamination solution. The solution is circulated until the concentration of metal ions in the solution leaving the cooling system is not substantially greater than the concentration of metal ions in the solution entering the cooling system.

After the metal ion-EDTA complex has been removed, the EDTA and any remaining ions in the solution can be removed by passing the solution through a fresh anion exchange resin or a mixed anion-cation exchange resin, which results in relatively pure water. When the preloaded anion exchange resin has been saturated with the metal ion-EDTA complex, it is disposed of as radioactive waste.

The invention will now be illustrated with reference to the following Examples: -

EXAMPLE 1

A 1 inch diamter glass column 18 inches long was partially filled with 100 ml of an anion exchange resin sold by Rohm and Haas under the trade designation "IRA-400," a strong-based polystyrene resin having a particle size between 16 and 50 mesh. A solution was prepared of 100 grams/liter of the disodium salt of EDTA. The solution, which had a pH of 4.38, was fed through the top of the column at 1-3 bed volumes/hr. and the pH of the solution leaving the bottom of the column was measured. The following table gives the pH of the solution leaving the column after various bed volumes of the solution had flowed through the column.

BED VOLUME	pH
0.5	11.85
1.0	12.86
1.5	12.94
2.0	12.36
2.5	6.56
3.0	5.90
3.5	5.64
4.0	5.47
4.5	5.29
5.0*	5.15
6.0	5.07

*A new solution was prepared having a pH of 4.49.

The above table shows that, after an initial start-up time, the pH of the solution leaving the resin fell to close to the pH of the solution entering the resin. This indicated that the column was almost saturated with EDTA.

EXAMPLE 2

Simulated spent decontamination solutions were prepared by dissolving 50, 100, and 200 ppm of iron (from magnetite, Fe_3O_4) in three 0.5 weight percent solutions of a commercially available decontamination agent believed to be 30% citric acid, 30% oxalic acid, 40% EDTA, and containing an inhibitor believed to be thiourea. The three solutions were mixed in beakers with the preloaded anion exchange resin prepared in Example 1 at 54°C. After 5 hours the solutions were tested and were found to contain 3, 11, and 46 ppm of iron, respectively. This established that the EDTA-loaded anion exchange resin successfully removed iron from the solutions.

EXAMPLE 3

A 100-ml sample of the EDTA-loaded anion exchange resin prepared as in Example 1 was placed in a 1 inch glass column 18 inches long. A 0.5% solution of the commercially available decontamination agent (described in Example 2) which contained 80 ppm of iron was passed through the column at 12 bed volumes/hr. from top to bottom and the iron, oxalate, citrate, and EDTA concentrations in the solution leaving the column were measured. The following table gives their concentrations.

BED VOLUME	IRON (ppm)	OXALATE (mg/ml)	CITRATE (mg/ml)	EDTA (ppm)
Feed	80	1080	1000	1384
10 to 11	39	10	290	4100
20 to 21	35	10	760	4366
40 to 41	37	10	1370	3352
60 to 61	14	78 83	1340	2521
80 to 81	8.8	430 430	1130	1783
90 to 91	3.8	500	910	984
100 to 101	1.0	830	970	1332

The above table shows that, after an initial start-up period, the EDTA-loaded column successfully removed iron in the solution to levels below 10 ppm.

CLAIMS:

1. A method of removing transition metals from a solution containing a complexing agent having an equilibrium constant for the ferric ion complex formation reaction of at least 10^{22}, characterized by loading an anion exchange resin with said complexing agent or a salt thereof and circulating said solution through said anion exchange resin.

2. A method according to claim 1, characterized in that the complexing agent is ethylene diamine tetraacetic acid or an alkali metal salt thereof.

3. A method according to claim 1 or 2, characterized in that the anion exchange resin is loaded by passing a solution of the salt of the complexing agent through said resin until the pH of said solution leaving said resin is less than 6.

4. A method according to claim 1, 2 or 3 characterized in that the transition metal is the ferric ion.

5. A method according to claim 1, 2 or 3, or 4, characterized in that the temperature of the solution is maintained at from 40 to 100°C.

6. A method according to any of claims 1 to 5, characterized in that the solution also contains citric acid and oxalic acid.

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EUROPEAN SEARCH REPORT

0135276

Application number
EP 84 30 4725

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)
1	X	GB-A-2 077 482 (US DEPARTMENT OF ENERGY) * claims 1-9 * -----	1-9	G 21 F 9/00

TECHNICAL FIELDS SEARCHED (Int. Cl.4)
G 21 F

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	01-11-1984	NICOLAS H.J.F.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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