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ION EXCHANGE PROCESS

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This invention is related to a process for removing ions from highly alkaline waste liquors. More particularly this invention is related to a process for removing radioactive cesium and strontium from highly alkaline waste liquor.

In the Purex process for recovering fissile values from spent nuclear fuel elements the fuel element is dissolved in nitric acid with subsequent separation of uranium and plutonium from the fission products, whereby the fission products are retained in a nitric acid solution which solution is a waste liquor. This waste liquor is then neutralized by the addition of excess sodium hydroxide, sufficient excess of sodium hydroxide being added to render the waste liquor highly alkaline. The neutralization of the waste liquors causes most of the fission products to be precipitated out of solution leaving a supernatant liquid containing radioactive cesium and trace amounts of other fission products such as strontium.

It has been proposed to remove the cesium and other radioactive ions from the highly alkaline radioactive supernatant waste liquor by contacting the liquor with a zeolitic ion exchange material to cause the radioactive cesium to exchange out of the liquor onto the ion exchange material. However, zeolitic ion exchange materials are seriously attacked upon contact with highly alkaline solutions. Furthermore, it is necessary for efficient cesium exchange onto zeolitic materials that a highly alkaline solution be used. Thus the art has sought a method of circumventing the problem posed by the degradation of the sieves in highly alkaline solutions.

It is an object of this invention to provide a process for protecting zeolitic materials from attack when they are contacted with highly alkaline materials without impairing ion exchange capacity of the zeolitic material.

It is an object of this invention to provide those skilled in the art with an efficient economic method of recovering radioactive cesium from highly alkaline waste liquor.

This and other objects of this invention will in part be obvious and will in part be shown hereinafter.

We have discovered an ion exchange process in which zeolitic ion exchange materials are protected from attack when the materials are in contact with strongly alkaline aqueous solutions comprising raising the aluminum ion content of the alkaline solution to at least about 0.04 mole per liter by the addition of a soluble aluminum bearing compound, e.g., sodium aluminate (Na_2AlO_2) to the alkaline solution prior to contacting the zeolitic material with the alkaline solution.

Further we have noted that when the use of ammonium carbonate ($(\text{NH}_4)_2\text{CO}_3$) as an elution agent to remove ions which have been exchanged out of our novel aluminum containing alkaline waste solutions onto the zeolitic material causes the formation of a white precipitate in the column upon reintroduction of further waste solution into the column after the elution of the radioactive ions from a previous batch. We have discovered that this can be avoided by washing the zeolitic material with an aqueous solution containing at least 8 moles of ammonium hydroxide per liter, after the elution step and prior to the reintroduction of further aluminum containing highly alkaline radioactive waste solutions into the column.

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By the term highly alkaline radioactive wastes we mean aqueous waste liquors having radioactive isotopes contained therein and also containing strongly alkaline materials, e.g., sodium hydroxide in amounts greater than about 0.45 mole per liter.

In the preferred embodiment of our invention we have discovered a process for the decontamination of highly alkaline radioactive aqueous wastes in which a zeolitic ion exchange material is used in an ion exchange column to remove cesium and strontium, to wit, a method of preventing chemical attack on and degradation of the said molecular sieve, comprising: preparing treated waste by incorporating sodium aluminate into said waste solution to a concentration of at least 0.04 molar; pretreating the zeolitic material with about 8 molar ammonium hydroxide; contacting the pretreated zeolitic material with the aluminate containing wastes; washing said contacted zeolitic material with water to remove any of said treated waste; contacting said washed zeolitic material with 0.2 molar ammonium carbonate solution to elute sodium; treating said contacted zeolitic material with 2 molar ammonium carbonate solution to elute cesium; and, washing said treated zeolitic material with water to remove all traces of ammonium carbonate prior to pretreating said zeolitic material with said ammonium hydroxide preparatory to further contacting of the zeolitic material with waste having aluminum incorporated therein.

The zeolitic materials useful in our novel process are well known to those skilled in the art. Alumino silicates which are suitable for use in our novel process can be natural or synthetic zeolitic type materials such as sodium alumino-silicate, sodium calcium alumino-silicate, calcium alumino-silicate, potassium alumino-silicate, cadmium alumino-silicate, strontium alumino-silicate, copper alumino-silicate, zinc alumino-silicate, cobalt alumino-silicate, iron alumino-silicate, silver alumino-silicate, nickel alumino-silicate, mixed alumino-silicates and naturally occurring or synthetically prepared phacalite, gmelinite, harmotome, analcite, chazbite and the like, or various base exchange modifications of these zeolites. Some of them, e.g., a sodium calcium alumino-silicate such as the one manufactured by the Linde Air Products Company and designated in the trade as "Linde AW400 Molecular Sieve" are preferentially used in our process.

The following examples are given to illustrate the practice of our invention.

In all examples an aqueous solution of the composition was employed.

Waste component:	Molarity
Na_2CO_3 -----	0.335
Na_2SO_4 -----	0.055
NaOH -----	0.47
NaNO_2 -----	0.90
NaNO_3 -----	1.60
CsNO_3 -----	.0005
SrCO_3 -----	1×10^{-6}

EXAMPLE I

A glass column having a length of 40 cm. and a diameter of 1 cm. was loaded to a depth of about 20 cm. with Linde AW400 Molecular Sieves R and the waste solution was pumped down through the column at a rate of about 33 cc. per hour until about 615.5 cc. of the solution had been pumped through the column. At this point a 1% breakthrough of cesium occurred. About 49.5 cc. of water was pumped upward through the column to remove any residual waste solution from the column. Thereafter 66 cc. of 0.2 molar $(\text{NH}_4)_2\text{CO}_3$ was pumped down through the column to elute cesium from the column.

During the water wash fine particles resulting from chemical attack and crumbling of the Molecular Sieves were observed in the effluent from the column.

EXAMPLE II

This example was performed in the same manner as Example I except that 0.023 mole/liter of Na_2AlO_2 were added to the waste solution. 584 cc. of this waste solution was passed through the column before a 1% cesium breakthrough occurred. The further procedures of Example I were carried out. In this example, fines again appeared in a lesser amount in comparison to Example I in the effluent during the washing step.

EXAMPLE III

This example was performed in the same manner as Example I except that 0.575 mole/liter of Na_2AlO_2 were added to waste solution and 531 cc. of waste solution was passed through the column before a 1% cesium breakthrough occurred. Following the elution steps of Example I the column was rinsed with water and fresh waste was passed down through the column. There was no observable attack for crumbling of the spheres at this point. After about 16.5 cc. of fresh waste was passed through the column a gelatinous white precipitate formed in the bed portion of the column.

EXAMPLE IV

In this example, Example III was duplicated except that at the end of the rinse step following the elution steps 165 cc. of 8 molar NH_4OH was passed down through the column prior to the reintroduction of 531 cc. of waste down through the column. There was no evidence of either crumbling or precipitation in the bed throughout the performance of this example.

Thus it will be obvious that our novel process provides an efficient economical method of removing cesium and strontium from highly alkaline radioactive wastes by the use of an ion exchange process utilizing commercially

available materials. Our process protects the physical integrity of the zeolitic material thus permitting reuse of this material.

We claim:

- 5 1. In an ion exchange process wherein strongly alkaline solutions are contacted with a zeolitic alumino-silicate ion exchange material, the improvement comprising preventing the chemical attack on and degradation of said ion exchange material by raising the aluminum ion content of the alkaline solution to at least about 0.04 mole per liter by the addition of a soluble aluminum bearing compound to the alkaline solution prior to contacting the zeolitic material with the alkaline solution.
- 10 2. In a process for the decontamination of highly alkaline radioactive aqueous wastes in which a zeolitic alumino-silicate ion exchange material is used in an ion exchange column to remove cesium and strontium the improvement of preventing chemical attack on and degradation of the said exchange material, comprising: preparing treated waste by incorporating sodium aluminate into said waste solution to a concentration of at least 0.04 molar; pretreating the zeolitic material with the aluminate containing wastes; washing said contacted zeolitic material with water to remove any of said treated waste; contacting said washed zeolitic material with 0.2 molar ammonium carbonate solution to elute sodium; treating said contacted zeolitic material with 2 molar ammonium carbonate solution to elute cesium; and, washing said treated zeolitic material with water to remove all traces of ammonium carbonate prior to pretreating said zeolitic material with said ammonium hydroxide preparatory to further contacting of the zeolitic material with waste having aluminum incorporated therein.
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