UNCLASSIFIED
(CLASSIFICATION)

GENERAL ELECTRIC

HANFORD ATOMIC PRODUCTS OPERATION - RICHLAND, WASHINGTON

DOCUMENT NO.

HW-84105

COPY NO.

TITLE

REMOVAL OF CESIUM FROM REDOX ALKALINE SUPERNATANT WASTES
BY ION EXCHANGE

DATE

10-1-64

ISSUING FILE

AUTHOR

K. C. KNOLL

MASTER

ROUTE TO

PAYROLL NO.

LOCATION

FILES ROUTE
DATE

SIGNATURE AND DATE

PATENT CLEARANCE OBTAINED. RELEASE TO
THE PUBLIC IS APPROVED. PROCEDURES
ARE ON FILE IN THE RECEIVING SECTION.

UNCLASSIFIED
(CLASSIFICATION)

UNCLASSIFIED

HW-84105

REMOVAL OF CESIUM FROM REDOX ALKALINE SUPERNATANT WASTES
BY ION EXCHANGE

By
K. C. Knoll^{1/}

Process Research and Development
Chemical Effluents Technology
CHEMICAL LABORATORY

HANFORD LABORATORIES

October 1, 1964

HANFORD ATOMIC PRODUCTS OPERATION

General Electric Company
Richland, Washington

^{1/} General Electric Company, Richland, Washington.

Work performed under Contract No. AT(45-1)-1350 between General Electric Company and the U.S. Atomic Energy Commission.

UNCLASSIFIED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

DISTRIBUTION

1. G. J. Alkire	18. R. L. Moore
2. S. J. Beard	19. J. L. Nelson
3. O. F. Beaulieu	20. A. M. Platt
4. R. E. Burns	21. R. P. Popovich
5. H. L. Caudill	22. H. C. Rathvon
6. E. W. Christopherson	23. R. L. Schmidt
7. W. V. DeMier	24. L. C. Schwendiman
8. W. A. Haney	25. O. V. Smiset
9. K. M. Harmon	26. P. W. Smith
10. E. R. Irish	27. S. G. Smolen
11. R. E. Isaacson	28. W. H. Swift
12. B. F. Judson	29. R. E. Tomlinson
13. R. L. Junkins	30. E. E. Voiland
14. A. R. Keene	31. M. T. Walling
15. K. C. Knoll	32. 300 Files
16. C. E. Linderoth	33. Record Center
17. B. W. Mercer	34-56. Extra

HANFORD ATOMIC PRODUCTS OPERATION
RICHLAND, WASHINGTON

NOTICE!

This report was prepared for use within General Electric Company in the course of work under Atomic Energy Commission Contract AT-(45-1)-1350, and any views or opinions expressed in the report are those of the authors only. This report is subject to revision upon collection of additional data.

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, express or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission to the extent that such employee or contractor prepares, handles or distributes, or provides access to, any information pursuant to his employment or contract with the Commission.

UNCLASSIFIED

REMOVAL OF CESIUM FROM REDOX ALKALINE SUPERNATANT WASTES
BY ION EXCHANGE

by

K. C. Knoll

INTRODUCTION

The removal of long-lived heat producing fission products from the high level wastes of the Purex and Redox plants is an integral part of the Chemical Processing Department Waste Management Program⁽¹⁾. A flow sheet was developed and a process demonstrated for the use of ion exchange techniques in the removal of Cs^{137} from Purex-type alkaline wastes⁽²⁾. In order to use this method with Redox-type wastes, it is necessary to modify the flow sheet because of the difference in waste composition, chiefly the presence of large quantities of aluminum in the Redox waste. This document describes a flow sheet using Duolite C-3 phenolic resin^(R) to remove cesium from Redox alkaline supernatant waste. The flow sheet is based on experimental results obtained with both synthetic waste and actual Redox supernatant waste.

SUMMARY

A flow sheet was developed for separating cesium from Redox alkaline waste supernate which uses Duolite C-3 resin as an ion exchange material. The waste is diluted with three parts of water and loaded onto the resin column at 25C, at a flow rate of 2 column volumes an hour. The column is washed with water to

(R) Diamond Alkali Co., Redwood City, California.

remove all waste solution and the cesium is then eluted from the resin with $3N$ $(NH_4)_2CO_3 \cdot 1 N NH_4 OH$. The resin is regenerated in the column with sodium hydroxide which also increases the pH of the bed to prevent aluminum hydroxide precipitation upon further contact with the waste. The resin is then ready for reloading. This flow sheet worked successfully with synthetic waste and with supernate from the Redox 115-SX tank.

The radiation stability of the C-3 resin was measured by loading a sample with about 5 curies of Cs^{137} . After 14 days the cesium was eluted and the irradiated resin, along with a control resin column, was loaded with Cs^{137} . About 15 percent loss of capacity was observed for the test column. The radioactivity to which the resin in the test column was exposed was greater than that to which it would be subjected in plant practice by a factor of 3000.

METHODS

Development work on the flow sheet for extracting cesium from Redox waste supernate was done with a synthetic waste with the composition shown in Table I.

TABLE I

Make-up of Synthetic Redox Alkaline Waste

<u>Compound</u>	<u>Molarity</u>
NaOH	8.6
NaNO ₃	0.20
NaNO ₂	0.70
NaCl	0.16
Na ₂ SO ₄	0.06
Al(NO ₃) ₃	1.7
CsCl	100%
KNO ₃	5.6×10^{-4}
RbCl	5.4×10^{-5}

The waste was made up as a dilute solution (1 volume of waste to 3 volumes of water) to prevent heavy precipitation as the solution cooled and aged.

Duolite C-3 is received in the hydrogen form, so it is necessary to convert it to the sodium-based form before using. If any hydrogen is left on the resin it will lower the pH of the influent waste enough to cause precipitation of aluminum hydroxide in the column with subsequent plugging

Several methods were tried to assure complete sodium basing. The most successful was a series of several cyclings between acid and base. A solution of 1.5 N HCl was pumped through the resin in a large column; the column contents were then washed with distilled water and then treated with 2N NaOH. This treatment was repeated four times, and the column was allowed to stand overnight filled with 8N NaOH. All washings were done with distilled water to prevent calcium from blocking any of the exchange sites. The sodium-based resin was air-dried and sieved, and the fraction between 20 and 50 mesh was used in the columns.

The experimental work was done with glass columns 0.8 cm I.D. and 20 cm long. This gave a column volume of 10 cm³ which contained 4 grams of sodium-based Duolite C-3. The columns were submerged in a temperature-regulated water bath and kept at 25C during loading and 55C during elution. The loading and eluting solutions were pumped through the columns at a rate of 2 cv/hr.

A 250 ml sample of supernatant waste from the Redox 115-SX tank was obtained from the Chemical Processing Department. A 750 ml portion of hot water

was used to dilute the sample and rinse out the sample bottle and transfer lines. The diluted waste (pH 12.3 Na 3.1 M) was passed through a glass column containing 2g of Duolite C-3 resin. Samples of the effluent were taken at intervals and the radioactivity present was measured with a gamma spectrometer.

Radiation stability was studied in a column of Duolite C-3 which remained loaded with Cs^{137} for 14 days. The column, 5 cm long and 1.6 cm in diameter, was filled with 4.4g of Duolite C-3, 40-60 mesh which had been sodium based. Feed for the column was a solution 2.1×10^{-3} M in cesium which had been produced by the scavenging of cesium from the 241-A-103 Purex tank supernate by the nickel ferrocyanate process. This solution was passed through the column until approximately 5 curies of Cs^{137} had been loaded on the exchanger. Distilled water was then pumped through the column continuously for 14 days to carry off any degradation products that might be formed. The cesium was eluted with ammonium carbonate. The resin was then reloaded with cesium to measure any change in capacity of the Duolite C-3 because of the radiation to which it had been exposed. At the same time a similar column of fresh C-3 was loaded with Cs^{137} from a synthetic waste under the same conditions, except for the 14 day wash, for comparison purposes. The Duolite C-3 in the test column received 380 curie hour/gram, while in plant operation the resin would be expected to receive 0.13 curie hour/gram.

RESULTS

Choice of Exchanger

Duolite C-3 was chosen for use after comparing it with Linde AW-400^(R) and AW-500^(R) and clinoptilolite, a natural zeolite. These exchangers were loaded

^(R) Linde Co., Tonawanda, New York.

with Cs^{137} contained in a synthetic waste and then eluted with ammonium carbonate solution. The loading and elution curves for all exchangers were compared. The AW-500 has a greater capacity than C-3 except at loadings below 5 percent (Figure 1). An advantage of C-3 is seen in Figure 2 where the elution curve shows that C-3 is 99 percent eluted at 2.5 column volumes while AW-500 is eluted only half as much at this point. On the basis of this ease of elution as well as its capacity, Duolite C-3 was chosen as the best exchanger for plant use.

Flow Sheet

The flow sheet used (Figure 3) was similar to the one developed for Purex waste⁽²⁾ with modifications to overcome the difficulties presented by the aluminum in the Redox waste. The resin in the column was loaded to about 1 percent capacity by pumping about 60 column volumes through at 2 cv/hr, at a temperature of 25C. The resin was then washed at the same rate with 10 cv of distilled water. This displaced any waste solution remaining in the column so that the $\text{Al}(\text{OH})_3$ would not precipitate when the lower pH eluting solution entered. Eight column volumes of $3\text{N}(\text{NH}_4)_2\text{CO}_3 \cdot 1\text{N} \text{NH}_4\text{OH}$ at 55C were pumped through to elute the cesium. The resin column was then ready to be regenerated for reuse.

Regeneration was accomplished by passing 3 cv of $2\text{N} \text{NaOH}$ through the column at 2 cv/hr and then recycling 4 cv of $8\text{N} \text{NaOH}$ through the column for 4 hours at 2 cv/hr. The column was then ready to be reloaded with waste. Figure 4 gives the breakthrough curves for three loading-eluting-regenerating cycles of a column of C-3 with synthetic waste.

Figure 1

Cesium Loading on Different Exchangers

Column: 0.8 cm I.D. 20 cm long.

Influent: Synthetic SX Supernatant
Diluted 1:1 25C

Column Filling:

8g Clinoptilolite	20-50 mesh
8g Linde AW 400	20-50 mesh
8g Linde AW 500	20-50 mesh
4g Duolite C-3	20-50 mesh

Flow Rate: 2 cv/hr

Figure 2

Elution of Cesium from Ion Exchangers

Columns: Loaded Columns from Figure 1

Eluant: $6N (NH_4)_2CO_3 + 2N NH_4OH$ 55°C

Flow Rate: 2 cv/hr

-6-

Figure 3

Flow Sheet for Cesium Extraction from Redox Alkaline Supernate
Waste with Duolite - C-3 Resin

HM-84105

Figure 4

Three Cycles of Column Loading with NaOH Downflow Regeneration

Column: 0.8 cm I.D. by 20 cm long.

Eluant: $3N(NH_4)_2CO_3$ · $1N NH_4OH$

Column Filling: 4g Duolite C-3 16-50 mesh.

Regeneration: ^{55°C} 8N NaOH 4 cv. Re-cycled 4 hours.Influent: Synthetic SX Supernatant.
Diluted 1:3 25°C

Flow Rate: 2 cv/hr.

The sodium-cesium ratio in the product of the first cycle was 580. The sodium-cesium ratio in the influent was 90,500.

Actual Waste Run

Supernate from the Redox 115 SX tank was run through a column which was treated to a load-elute-regenerate cycle three times. The resulting loading curves are shown in Figure 5. Because of the limited volume of solution available only a small amount could be put through on each cycle so only a few samples could be taken.

These results can be compared with the breakthrough curves for synthetic Redox waste supernate as shown in Figure 4. The 1 percent breakthrough points for actual waste are not quite as good as, but are still comparable with, those for synthetic waste. The column through which the actual waste passed was small, which does not give as consistent results as the larger columns used with synthetic waste.

Operating Characteristics of Columns

A column was set up to recycle the synthetic SX waste a number of times to observe losses of resin and cesium. After 18 successive cycles less than 5 percent by weight of the Duolite C-3 had been lost. The amount of Cs¹³⁷ lost through the washes of the column was measured over 12 cycles and was found to be less than 0.1 percent.

Pressure drop across a C-3 bed was measured and found to be minimal. The results are given in Table II.

Figure 5

Three Cycles of Loading of Actual Redox Waste onto Duolite C-3

Column: 1 cm I.D. x 6.4 cm long.

Eluant: $3N(NH_4)_2CO_3$. $1N NH_4OH$
55CColumn Filling: 2g Duolite C-3 20-50
mesh.Regeneration: Alternate washes of 3 cv
 $2N NaOH$ and $2N H_2SO_4$ recycled
3 times.Influent: Supernatant from Redox 115 SX
Tank - Diluted 1 to 3 25CFinal Wash. 35 cv - $2N NaOH$

-13-

TABLE II

Pressure Drop Across a C-3 Bed at 2 cv/hr Flow
for Water and Synthetic 1:1 SX Supernate

<u>Mesh Size</u>	<u>Solution</u>	<u>Pressure Drop</u> <u>Feet Water/Foot Bed Length</u>
20-40	Water	0.02
	SX	0.46
40-60	Water	0.62
	SX	> 20.
20-60	Water	0.23
	SX	0.59

When the effect of particle size of C-3 was studied, a slight gain in capacity at 1 percent breakthrough was observed as was expected⁽²⁾. This is shown in Table III.

TABLE III

Effect of Particle Size on 1% Breakthrough

<u>Particle Size</u>	<u>Column Volumes</u>
20-40	7.1
40-60	11.0
20-60	10.0

Radiation Stability

There was no evidence of serious deleterious effects on the Duolite C-3 from its exposure to radiation. More than 99 percent of the cesium which had been loaded on the resin was eluted, showing the exchanged ion could be readily removed after irradiation. Breakthrough curves of the reloading of the irradiated

and control columns are given in Figure 6. This shows a loss of about 15 percent of the capacity of the resin for cesium after irradiation. Examination of irradiated and unirradiated resin under a microscope showed no difference in appearance between the two. Crushing tests showed there was no noticeable softening of the irradiated material. This resin was subjected to more rigorous conditions than will be the case in plant practice. These results indicate adequate capability to withstand radiation damage, making Duolite C-3 suitable for plant use.

ACKNOWLEDGMENT

The author wishes to acknowledge the help given by Mr. R. L. Schmidt for his work in the laboratory and his many helpful suggestions made in the course of the investigation.

REFERENCES

1. S. J. Beard, and R. J. Kofoed. "Waste Management Program - C.P.D." HW-81481. March, 1964.
2. J. L. Nelson, and B. W. Mercer. "Ion Exchange Separation of Cesium from Alkaline Waste Supernatant Solutions," HW-76449, January, 1963.

Figure 6
Loading of Irradiated and Unirradiated Duolite C-3

Column: 1.6 cm I.D. x 5 cm long

Influent: Synthetic SX supernatant
Diluted 1:1 25C

Column Filling: 4.4g Duolite C-3
20-50 mesh

Flow Rate: 2 cv/hr.