3

664354

DP-973

AEC RESEARCH AND DEVELOPMENT REPORT

DEPLETION OF DEIONIZER RESIN IN AN SRP REACTOR SYSTEM

E. W. Baumann

RECORD COPY
DO NOT RELEASE
FROM FILE

DU PONT
REG. U. S. PAT. OFF.

Savannah River Laboratory

Aiken, South Carolina

Printed in USA. Price $1.00
Available from the Clearinghouse for Federal Scientific
and Technical Information, National Bureau of Standards,
U. S. Department of Commerce, Springfield, Virginia

664354

DP-973

Reactor Technology
(TID-4500, 43rd Ed.)

DEPLETION OF DEIONIZER RESIN IN AN SRP REACTOR SYSTEM

by

Elizabeth W. Baumann

Approved by

E. L. Albenesius, Research Manager
Analytical Chemistry Division

August 1965

E. I. DU PONT DE NEMOURS & COMPANY
SAVANNAH RIVER LABORATORY
AIKEN, SOUTH CAROLINA

CONTRACT AT(07-2)-1 WITH THE
UNITED STATES ATOMIC ENERGY COMMISSION

ABSTRACT

An axial core section was removed from a depleted deionizer from an SRP reactor system, and the ion exchange resins were examined for absorbed ions, retained solids, and residual and regenerable exchange capacity. Total depletion of the initial capacity of the cation exchange resin was 60% and that of the anion exchange resin was 90%. Destruction of exchange sites by radiation and absorption of resin degradation products accounted for 30% of the depletion of each resin.

CONTENTS

LIST OF TABLES AND FIGURES

DEPLETION OF DEIONIZER RESIN
IN AN SRP REACTOR SYSTEM

INTRODUCTION

The examination of used resins is an important part of the study of the performance of deionizers in the heavy water purification system of Savannah River reactors. Such examination provides information about the ionic content of the heavy water moderator and the factors that contribute to deionizer depletion. Determination of the ionic content of moderator from ions concentrated on the resin supplements direct analysis of the moderator and establishes that major ionic impurities have been recognized. Investigation of the factors causing resin depletion indicates whether maximum usage is obtained from the deionizers, which are discarded when spent.

Most resins examined previously were obtained from a "miniature purification system", which consisted of small ion exchange columns in a reactor loop.(1,2) These resins provided good information about ions removed from moderator, but they could not provide information that directly corresponded with Plant operating conditions. In particular, indications that process resins were degraded during service, perhaps by radiation damage(3), could not be confirmed by testing in the small system. Knowledge of the condition of resin that had been used in the reactor purification system was therefore needed.

This report describes the sampling and examination of radioactive spent resin from a production deionizer and defines factors that contributed to depletion of the available exchange sites of the resin.

SUMMARY

An axial core of resin from a spent deionizer of a Savannah River production reactor was sampled with a specially designed tool. The cation and anion exchange resins were examined for absorbed ions and retained solids, and for evidences of resin degradation.

Total depletion of the initial capacity of the cation resin was 60%, while depletion of the anion resin was 90%. The resin depletion was attributed to the following mechanisms: (1) destruction of exchange sites by radiation, (2) absorption of degradation products of the resins, and (3) absorption of ions from the moderator.

Depletion of exchange capacity by the combination of mechanisms (1) and (2) amounted to 30% of the initial capacity for both cation and anion resins. An additional 30% of the initial capacity of the cation resin was depleted by absorption of cations from the moderator; one-half of this loss in capacity was due to the absorption of Al^{3+} that was probably produced when solid alumina filtered from the moderator was dissolved by the acid resin. These alumina particles, less than 2 microns in diameter, amounted to about 0.5 wt % of the resin. Anions, chiefly NO_3^- and DCO_3^-, absorbed from the moderator, occupied 60% of the initial exchange sites of the anion resin.

These results show that the deionizer systems are being operated under favorable conditions; however, some improvement in the service life of the resin could be realized if ion exchange materials with greater radiation resistance were available.

DISCUSSION

DESCRIPTION OF SYSTEM

The chemistry and the purification of SRP heavy water moderator has been described in detail elsewhere.(4,5) The moderator contains approximately 10^{-5} $\underline{M}$ DNO_3 (pD = 5) added to inhibit corrosion of aluminum components, plus suspended alumina and iron oxides, radionuclides from fission and neutron activation, and miscellaneous ionic impurities.

Table I gives the history of the deionizer that was sampled. The resin was a mixture with a nominal anion-to-cation equivalent ratio of 2:1. The anion exchange resin is of the quaternary ammonium type, originally in the OD^- form. The cation exchange resin is of the sulfonic acid type, originally in the D^+ form.

EXPERIMENTAL PROCEDURE

Sampling the Resin

The deionizer sample was believed to be representative of resin at the end of its service in the reactor system. The deionizer was still filled with heavy water when sampled and had undergone no treatment after it was taken off-line. The deionizer was not sampled until three months after it was removed from reactor service, to reduce radiation exposure to personnel during sampling and examination.

TABLE I

History of Deionizer

Length of service	85 days
Throughput	6.3×10^6 gallons
Average composition of feed	
Radioactivity (2-hr decay, beta count of evaporated mount, counting efficiency 5.7% with RaD-RaE standard)	250,000 c/m/ml
pD	5.1
Conductivity	2.4 µmhos/cm

Initial Resin (Resins mixed in deionizer):

	Cation Exchange Resin	Anion Exchange Resin
Pounds of moist resin	250	846
Exchange capacity, meq/ml	1.9	1.1
Exchange capacity, meq/g dry resin (used in calculations for Figure 2)	4.5	3.3

A core of resin along the vertical axis of the deionizer was obtained by the specially designed sampler shown in Figure 1. This all aluminum tool consisted of a central rod with spacers, covered by a removable sheath. In the sampling operation, the sheathed sampler was inserted to the bottom of the resin bed and the sheath was withdrawn to allow resin to enter the sampling spaces. The sheath was then replaced and the assembly was removed from the deionizer. Excess water from the resin sample was allowed to drain back into the deionizer.

The sampler was placed in a shipping container and brought to the laboratory where it was dismantled. Eight samples were recovered sequentially from between the spacers as the sheath was withdrawn, as shown in Figure 1.

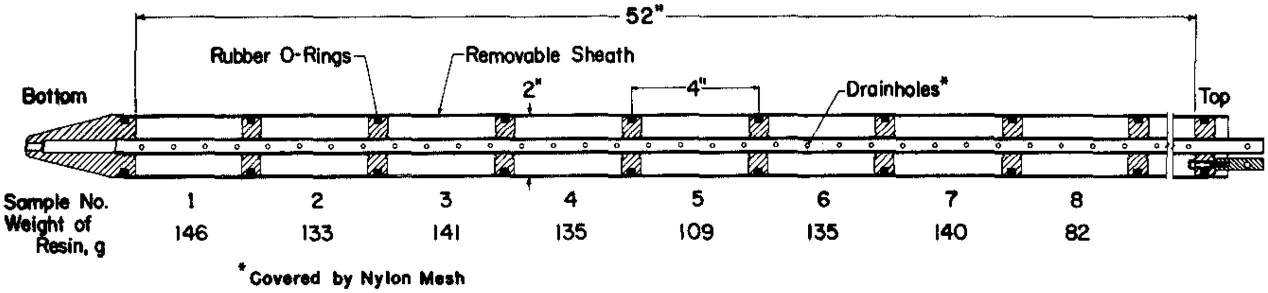

FIG. 1 TOOL FOR SAMPLING DEIONIZER

Examining the Resin

The mixed resin was treated by methods previously described.(1, 2, 6)

Separation of Filtered Solids - The resin samples were backwashed and the washings were filtered on a 0.45-micron "Millipore"* filter. The residue was dried over $CaSO_4$.

Separation of Cation and Anion Resin Components - The initial separation was made by water flotation. This separation was difficult because the differences in density and appearance were slight. A final separation was made in glycerine to obtain a clean cation resin fraction.

Analysis of Resins - The exchange capacities and the ions absorbed were determined on salt elutriates of the separated resin components.

RESULTS

Mixed Resin

Appearance - The resin was uniformly dark brown. The anion exchange resin, originally yellow, had darkened during service, due to radiation exposure. The physical state of the resin was good; the spherical beads were intact and firm.

Radioactivity - Figure 2 shows dose rates for the resins as they were removed from the sampler. A large proportion of the activity was shielded out by 3/8-inch transparent plastic, the "closed window" readings. The cation exchange resin contained most of the radioactivity.

Filtered Solids - During the initial backwashing of the resin with water, finely divided material that had been retained by the resin was released. The water was foamy, indicating the presence of some organic material. With continued washing of the resin, the water clarified rapidly.

Figure 2 shows the distribution of the solids along the column. The apparent concentration of solids at the center of the deionizer was not expected. Results of examination of the solids are given in

---

*Trademark of Millipore Filter Corporation, Bedford, Mass.

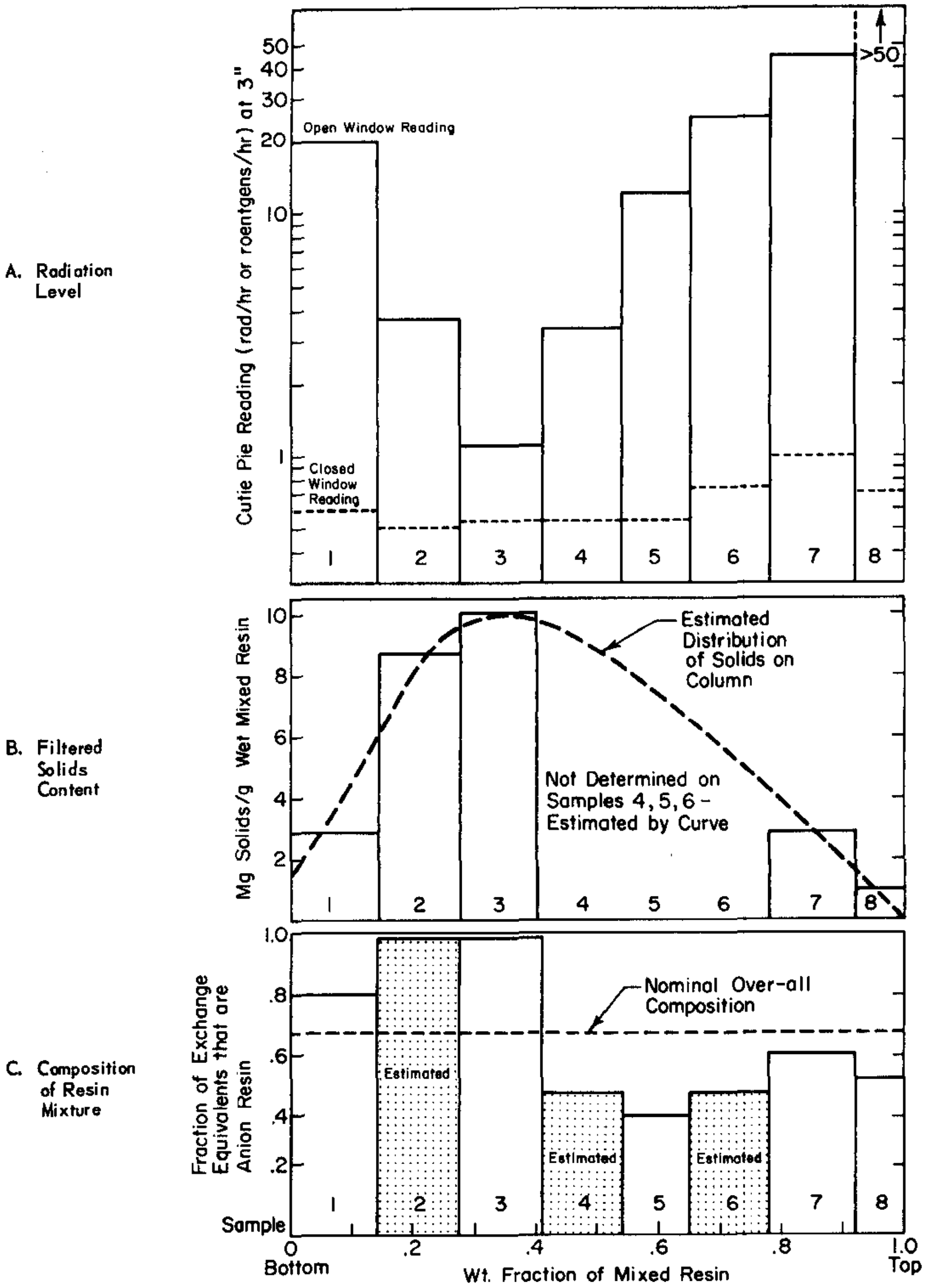

FIG. 2 CHARACTERIZATION OF MIXED RESIN

Table II. The material was mostly alumina, which is always found in water from this reactor system. The maximum particle size is limited by a 5-micron filter that removes the larger particles upstream of the deionizer. The resins thus supplement the filters by retaining very small particles, although their filtering action is not quantitative. The total amount of solids held (0.5 wt %) was slightly less than the 0.8 wt % observed in the earlier miniature purification tests; however, the present cross-sectional flow was nearly twice that of the earlier tests.

TABLE II

Solids Filtered on Resin

Amount	
Estimated average concentration	5 mg/g wet mixed resin (0.5 wt %)
Corresponding total amount in deionizer	5.5 lb
Nature	
Particle size range, estimated from electron photomicrographs	<0.01 to 2 μ
X-ray diffraction	β-$Al_2O_3 \cdot 3H_2O$ (Not too well crystallized) No other crystalline components
Cl content (by neutron activation method)	360 ppm

The chloride content of the alumina is similar to that usually found in alumina from the SRP reactor systems.

Composition of Resin Mixture - The composition of the original resin mixture was calculated by determining the total number of exchange equivalents of each resin in the mixture, and correcting for degradation by a factor obtained from analysis of the individual resins. Compositions of samples 2, 4, and 6 were estimated from visual observation and the nominal over-all composition of the deionizer mixture.

As shown in Figure 2, the mixture along the column was markedly nonuniform. Samples 2 and 3 contained practically no cation resin.

Individual Resins

Figure 3 illustrates the pattern of depletion of cation and anion resin exchange capacity for each sample along the length of the deionizer. Fractional depletion of the column as a whole by absorption of ions and by degradation is also given; the nonuniformity of the mixture has been taken into account.

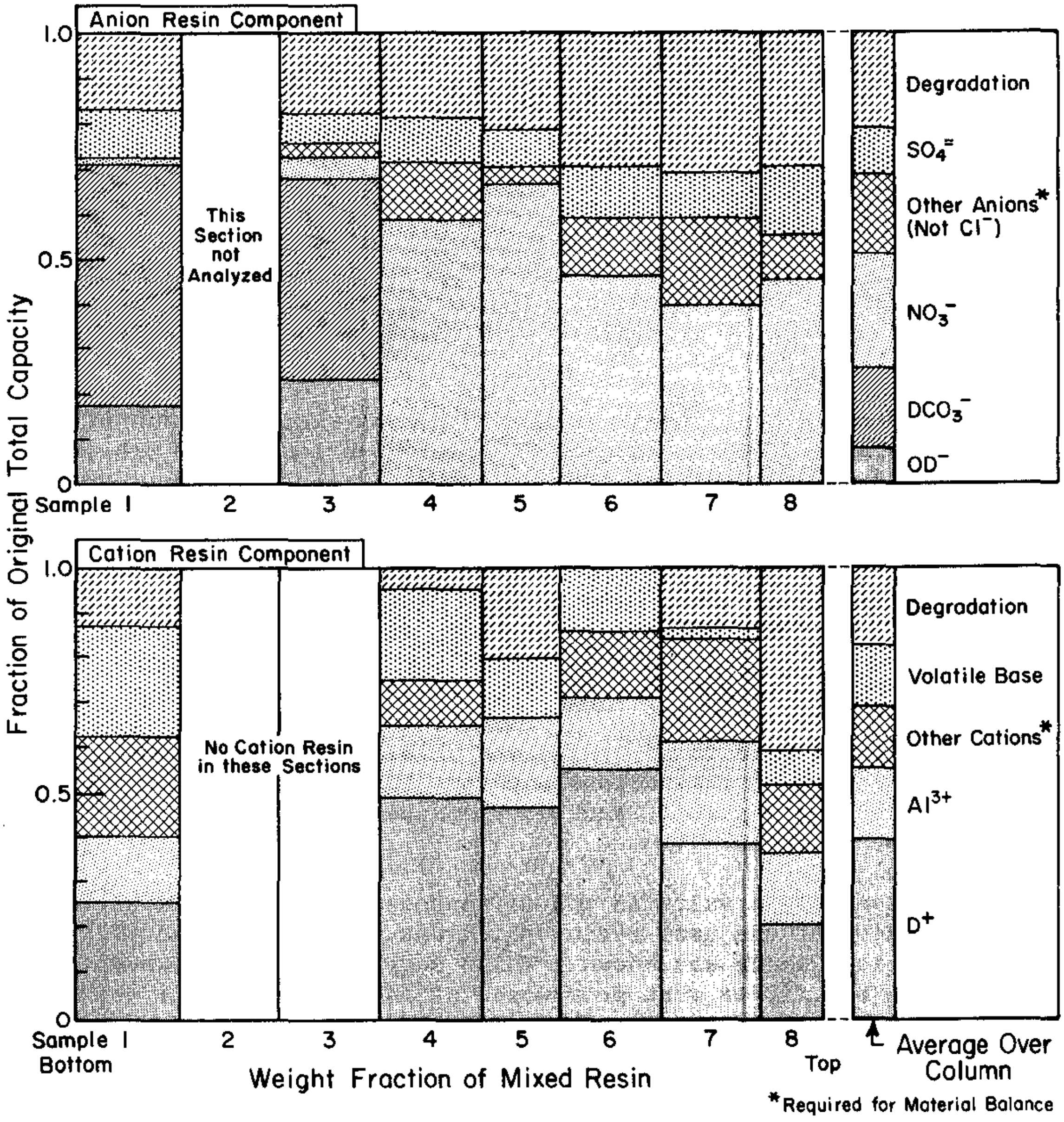

FIG. 3 PATTERN OF DEPLETION OF RESINS

Anion Resin

OD^- - Less than 10% of the anion exchange capacity of the column remained in the OD^- form; this residual was located at the bottom of the column.

DCO_3^- - Bicarbonate accounts for nearly 20% of the total exchange capacity. Its source is not known with certainty. A small amount of CO_2 may be absorbed from the air by the alkaline resin during deionizer preparation. However, most of the CO_2 is probably produced during service from radiolysis of organic material either within the deionizer or in the moderator. Displacement of DCO_3^- by NO_3^- occurs as would be predicted from selectivity of resin for these ions.

NO_3^- - Nitrate, from nitric acid added to the moderator, is the major exhausting ion at the top of the column. It accounts for about 25% of the total anion exchange capacity. This amount of NO_3^-, considered as DNO_3, corresponds to an average pD of 5.2 in the original moderator. Reasonable agreement of this value with the pD of 5.1 indicated from process data confirms that nitric acid is the principal acidifier.

Cl^- - The resin contained less than one equivalent per cent of Cl^-, which corresponds to an average Cl^- concentration of <10 ppb in the moderator during the period of operation.

$SO_4^=$ - Sulfate occupies about 10% of the exchange capacity. This ion is considered to have come from cation resin degradation rather than from impurities in the moderator because it is uniformly distributed throughout the bed. Had it been collected from the moderator, it would have been concentrated at the top of the bed because of the preference of the resin for this divalent anion.

Other Anions - This value, which was obtained by difference, reflects uncertainty of the various analyses and also suggests that small amounts of other anions, such as chromates, manganates, or aluminate, were present.

Degradation - This value is the difference between the total exchange capacity of the used resin, which was determined, and the original capacity, which was known. While degradation is apparent throughout the bed, it is most pronounced at the top where the most severely degrading radiation environment would have been encountered. The over-all degradation of the resin corresponds to about 20% of the total exchange capacity.

Cation Resin

D$^+$ - Nearly 40% of the original exchange capacity remained in the deuterium form. Since cationic contaminants in significant quantities do not occur in this acid moderator, exhaustion of the cation resin was not expected.

Al^{3+} - Aluminum ion accounts for 15% of the resin depletion and corresponds to an average Al^{3+} concentration in original moderator of about 10^{-6} molar, which is approximately the solubility of aluminum hydroxide. The depletion pattern with the aluminum ion distributed uniformly along the length of the column suggests, however, that aluminum did not come from soluble ions, but rather that it was absorbed by dissolution of the insoluble alumina by the resin, by the reaction

$$1/2\ Al_2O_3 \cdot 3H_2O + 3HRes \longrightarrow AlRes_3 + 3H_2O$$

Volatile Base - Volatile base, e.g., ammonia or trimethylamine, is presumed to be a product of anion resin degradation. Since in the present mixture cation resin is a minority component that absorbs the degradation product of a majority component, distribution of volatile base is strongly affected by the nonuniformity of the mixture. At the bottom of the column, where the proportion of anion resin was abnormally high, a large amount of volatile base was found. The skewness of the distribution toward the bottom of the column suggests that volatile base may have leaked from the column during service.

Other Cations - The 15% listed as other cations reflects the uncertainty of analyses as well as the probable presence of other cations, such as Mg, Ca, and Fe.

Degradation - As with the anion resin, degradation represented the difference between the total exchange capacity found and that of the original resin. The degradation pattern of the cation resin is somewhat erratic. At the top of the column the total exchange capacity was only 60% that of the original resin. This very large reduction in exchange capacity at the top of the bed was attributed to damage from oxidizing conditions coupled with the strong radiation dose, primarily from ^{24}Na which was continually collecting and decaying in this zone.

DISCUSSION OF RESULTS

The service life of the deionizer was limited by a 90% depletion of the anion resin. This high degree of exhaustion is in line with expectations for mixed-bed performance; however, only about 60% of the anion resin capacity was actually used for deionization of reactor moderator. Of the 60%, less than half was used in removal of nitrate, the only anion deliberately maintained in the moderator. The impurity, DCO_3^-, accounted for a large proportion of the remainder. Resin degradation accounted for the other 30% depletion. The exchange capacity of the anion resin was reduced by loss of exchange sites and by absorption of $SO_4^=$, a degradation product of the cation resin.

The total depletion of cation exchange capacity was about 60%. Of this, less than 15% was attributed to ions in the feed; dissolution of alumina by the resin accounted for another 15%. The remaining 30% was attributed to resin degradation.

The cause of the resin degradation has been attributed to radiation damage(3) since these resins accumulate a large dose from ^{24}Na removed from the moderator. This nuclide, produced by the reaction ^{27}Al (n,α) ^{24}Na, is indigenous to reactor systems containing aluminum and hence the radiation dose encountered by the resins in this system is substantially higher than in reactor systems that contain no aluminum. The presence of 10^{-5} $\underline{M}$ DNO_3 and 1-5 ppm D_2O_2 also contribute to a degrading environment, but their contribution is believed to be minor compared to that from the radiation.

Low usage of the bed for removal of ions from the moderator suggests the possibility of improvement, but changes that have been considered appear less practical or economical than allowing resin exhaustion from extraneous sources to proceed. The anion resin content of the bed is currently twice the cation resin; further increase in the proportion of anion resin would afford only a small increase in anion capacity and furthermore might compromise complete removal of cations. In the present instance, the nonuniformity of the mixture may have resulted in localized regions of inefficient deionization; more uniform mixtures are ordinarily attained. A process for reducing radiation dose by removing radioactivity upstream of the bed, e.g., by inorganic exchangers that are not subject to radiation damage, does not appear practical at this writing. Some improvement in service life of the resin could be realized if ion exchange materials with greater radiation resistance were available. Problems involved in scavenging dissolved $CO_2(DCO_3^-)$ by chemical stripping of CO_2 from the blanket gas appear to outweigh the possible advantage to be gained.

ACKNOWLEDGMENT

The sampling tool was designed by T. S. McMillan of the Savannah River Laboratory. The resin sample was obtained through the joint efforts of personnel from the Works Technical Department and the Production Department of the Savannah River Plant.

REFERENCES

1. E. W. Baumann. Miniature Purification Progress Report. I. Description of Equipment, Tests Ia, Ib, and II. USAEC Report DP-678, E. I. du Pont de Nemours & Co., Savannah River Laboratory, Aiken, S. C. (1962).

2. E. W. Baumann. Ibid. II. Tests III through VI. DP-806 (1962).

3. E. W. Baumann. Radiolysis of Ion Exchange Resins Used in the Purification Systems of Savannah River Reactors. USAEC Report DP-977, E. I. du Pont de Nemours & Co., Savannah River Laboratory, Aiken, S. C. (1965), and paper presented at the 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April 6-10, 1964.

4. F. B. Longtin. "Impurities in Moderator of Savannah River Plant Reactors," paper presented at the 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April 6-10, 1964.

5. G. N. Flannagan and R. F. Anderson. "Quality Control of Moderator in Savannah River Plant Reactors." Ibid.

6. E. W. Baumann. Analysis of Used Ion Exchange Resins. USAEC Report DP-218, E. I. du Pont de Nemours & Co., Savannah River Laboratory, Aiken, S. C. (1957).