662907

DP-1343

MERCURY REMOVAL FROM AQUEOUS PROCESS STREAMS

D. W. THARIN

E. I. du Pont de Nemours & Co.
Savannah River Laboratory
Aiken, S. C. 29801

PREPARED FOR THE U. S. ATOMIC ENERGY COMMISSION UNDER CONTRACT AT(07-2)-1

Printed in the United States of America
Available from
National Technical Information Service
U. S. Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22151
Price: Printed Copy $4.00; Microfiche $1.45

662907

DP-1343
UC-38

MERCURY REMOVAL FROM AQUEOUS PROCESS STREAMS

by

D. W. Tharin

A. R. McJunkin, Contributor

Approved by

E. B. Sheldon, Superintendent
Separations Technology Section

January 1974

E. I. DU PONT DE NEMOURS & COMPANY
SAVANNAH RIVER LABORATORY
AIKEN, S. C. 29801

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

ABSTRACT

A simple method for removing mercury from aqueous process streams has been developed. The system consists of a column packed with finely ground vulcanized rubber preceded by a liquid cyclone separator. In one test, a pilot-scale packed bed containing finely ground tire rubber produced an effluent having <10 ppb mercury for 170 bed volumes throughput, and <100 ppb for over 600 bed volumes. Feed solution contained 1800 to 11,000 ppb mercury in a dissolved or colloidal state. In batch laboratory tests, mercury was reduced from 750 ppb to less than 5 ppb in five minutes at 70°C.

The ability of rubber to capture mercury in almost any physical or chemical form over a wide range of pH and concentration provides an economical method for cleaning up waste effluent from many industrial sources. This process uses one waste product to control another and at a cost below that of previously described processes. The use of discarded tire rubber to absorb mercury may have wide application.

CONTENTS

LIST OF FIGURES

LIST OF TABLES

MERCURY REMOVAL FROM AQUEOUS PROCESS STREAMS

INTRODUCTION

At the Savannah River Plant, acidic radioactive wastes from processing reactor fuels and targets are neutralized with excess caustic and stored in mild steel tanks. Mercury enters these wastes from two sources: mercury is used as a catalyst in nitric acid solutions to dissolve aluminum alloy fuels, and it is present as an impurity (1500 ppb) in sodium hydroxide used for dissolving aluminum cladding from certain fuels and for neutralizing acid wastes.

After radioactivity in the stored aqueous waste has decayed to acceptable levels, the volume of the waste is reduced by evaporation. During evaporation, some of the mercury compounds are reduced to elemental mercury, which steam-distills and condenses along with the water vapor. Also, some of the mercury is entrained by the steam. The condensate is discarded to earthen seepage basins after treatment to remove cesium-137. The total amount of mercury is about 0.5 lb/day in 15,000 gallons of water.

Mercury can be in the condensate as immiscible droplets; suspended, insoluble compounds; colloids; or ionic, dissolved mercury. The immiscible droplets and insoluble compounds can be removed by settling or centrifugation. The ionic form requires chemical removal. The colloids can be removed by either physical or chemical means. Micro-filtration normally will remove colloidal particles, which are 2 to 80 μm in diameter; however, these particles are charged and may react chemically much like ionic mercury.[1]

Small accumulations of elemental mercury have been observed in condensate (drained from low points in piping) and in analytical samples. These accumulations caused no concern in the past because the condensate goes to seepage basins that retain mercury, preventing it from reaching surface streams. However, recent general emphasis on minimizing of mercury releases to the environment[2-5] provided the impetus to determine the quantity of mercury in the condensate and to develop methods for removal, should the need arise.

DEVELOPMENT OF MERCURY REMOVAL COLUMN

EQUIPMENT AND EXPERIMENTAL METHOD

The first objective of the mercury removal program was to separate the easy-to-remove immiscible mercury from the condensate, thereby preventing any potential release to the environment. The second objective was to study various physical and chemical treatments for removing the remaining mercury in the condensate.

To achieve these objectives, an experimental mercury removal column was designed with two liquid-liquid cyclone separators in series and separated by a packed column (Figure 1). Installation of the mercury removal column in the evaporator overheads system is shown in Figure 2. All of the condensate was run through the first liquid cyclone separator to separate elemental mercury. The effluent, containing mercury in colloidal and ionic forms, could be diverted to study various methods to remove the remaining mercury.

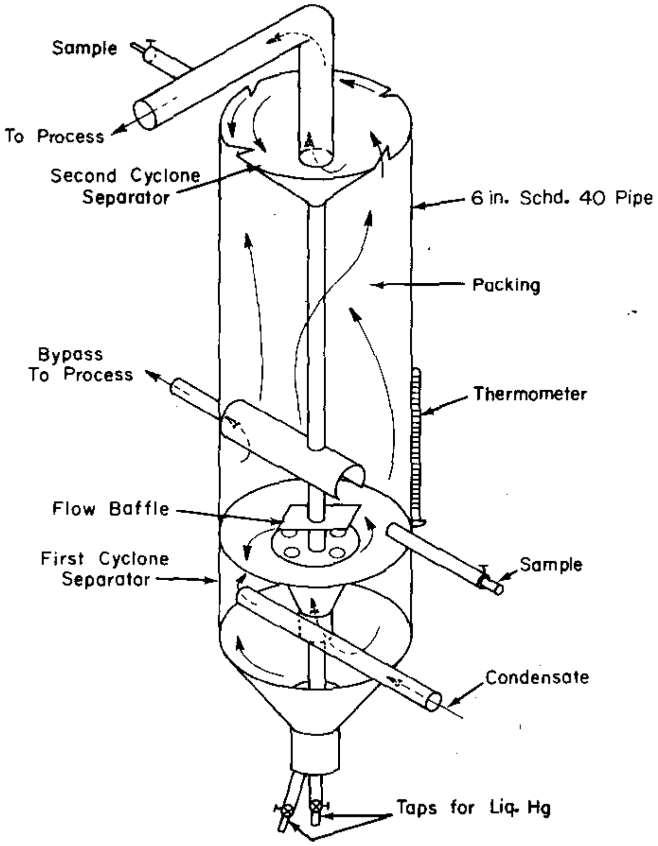

FIGURE 1. Mercury Removal Column

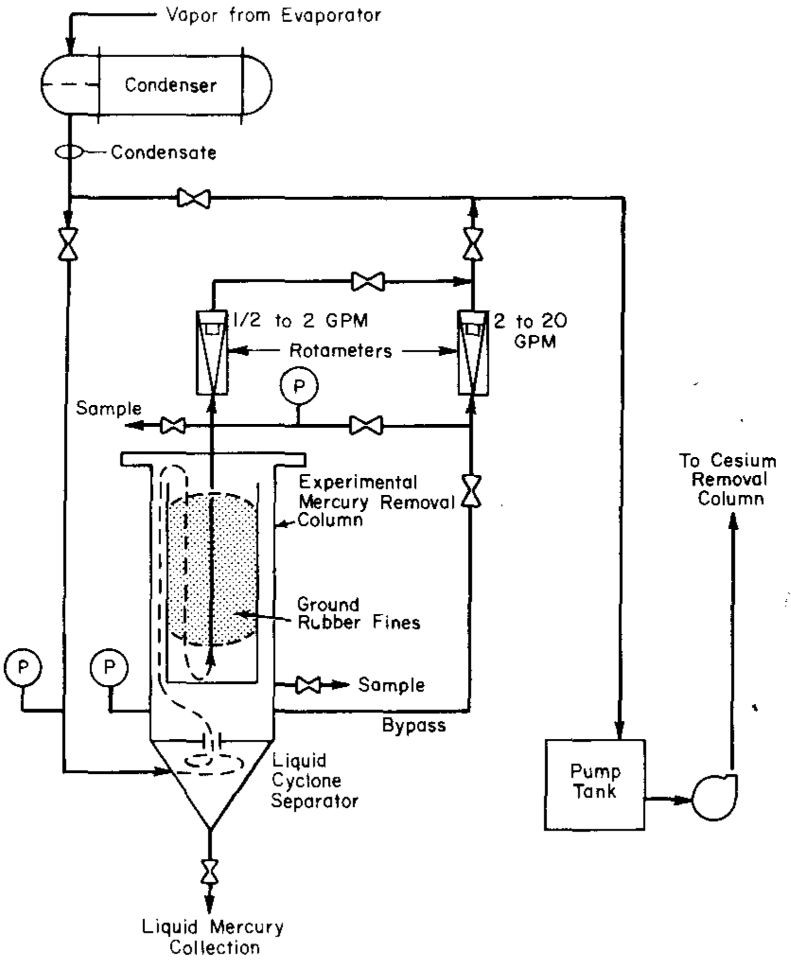

FIGURE 2. Flow Diagram for Experimental Mercury Removal Column (Shown in final down-flow configuration with upper cyclone separator removed)

The first cyclone separator was simply a 6-in. x 3-in. concentric pipe reducer with a tangential entry line and a concentric effluent duct. The second cyclone separator was a *Teflon**-coated funnel with tangential slits to impart spin to the liquid stream. There was no underflow drawoff from either cyclone separator during operation because the reservoir at the bottom of each separator was sufficient to contain the collected mercury. The mercury was drawn off daily and measured in a graduated cylinder. A transparent-plastic top end-plate permitted observation of the interior of the column during operation.

---

* Registered trademark of E. I. du Pont de Nemours and Co., Wilmington, Delaware.

A large 2 to 20 gpm effluent rotameter was equipped with a non-standard bob and was used for comparative readings only. For collection efficiency testing, flow through the packed section was measured by a 1/2 to 2 gpm rotameter, and total volume over a time period was calculated. Column effluent was collected in a calibrated vessel to determine flow rates when measuring condensate residence times in the column.

Overheads temperatures were determined by a mercury thermometer. Comparisons with readings from a nearby in-line process thermometer showed differences of only ±2°C.

All samples were taken in 8-ounce glass bottles containing approximately 1 cc of 50% HNO_3 to prevent mercury from plating out on the glass surfaces.

Mercury concentrations were determined by a cadmium sulfide exchange process followed by emission spectrographic analysis. This analytical technique was accurate to within ±10% in the concentration range of these tests. In the tests with ground rubber, samples were passed through a 0.4-μm-particle-collecting filter before analysis.

MERCURY REMOVAL BY CENTRIFUGATION

Cyclone separators were selected for centrifugal separation of mercury droplets. These separators can be operated continuously, they have no moving parts, and the components can be easily changed. For example, if higher spin velocity for the same flow rate is desired, the diameter of the inlet pipe can be reduced by an insert in the 1-inch inlet pipe. Also, the length and diameter of the overflow pipe can be changed easily to alter internal flow characteristics.

Initial flow tests on the mercury removal column were made without packing in the column to measure pressure drop and to determine the mercury removal by the cyclone separators alone. Pressure loss at 10 gpm was 0.2 to 0.3 psi through the first cyclone separator and about 1.0 psi through the second separator.

Mercury removal by the first cyclone separator was based on the volume accumulated at the operating temperatures of 65 to 80°C and is shown in Figure 3. No temperature correlation was obtained. The average mercury concentration was reduced from 510 to 350 ppb by the second cyclone separator.

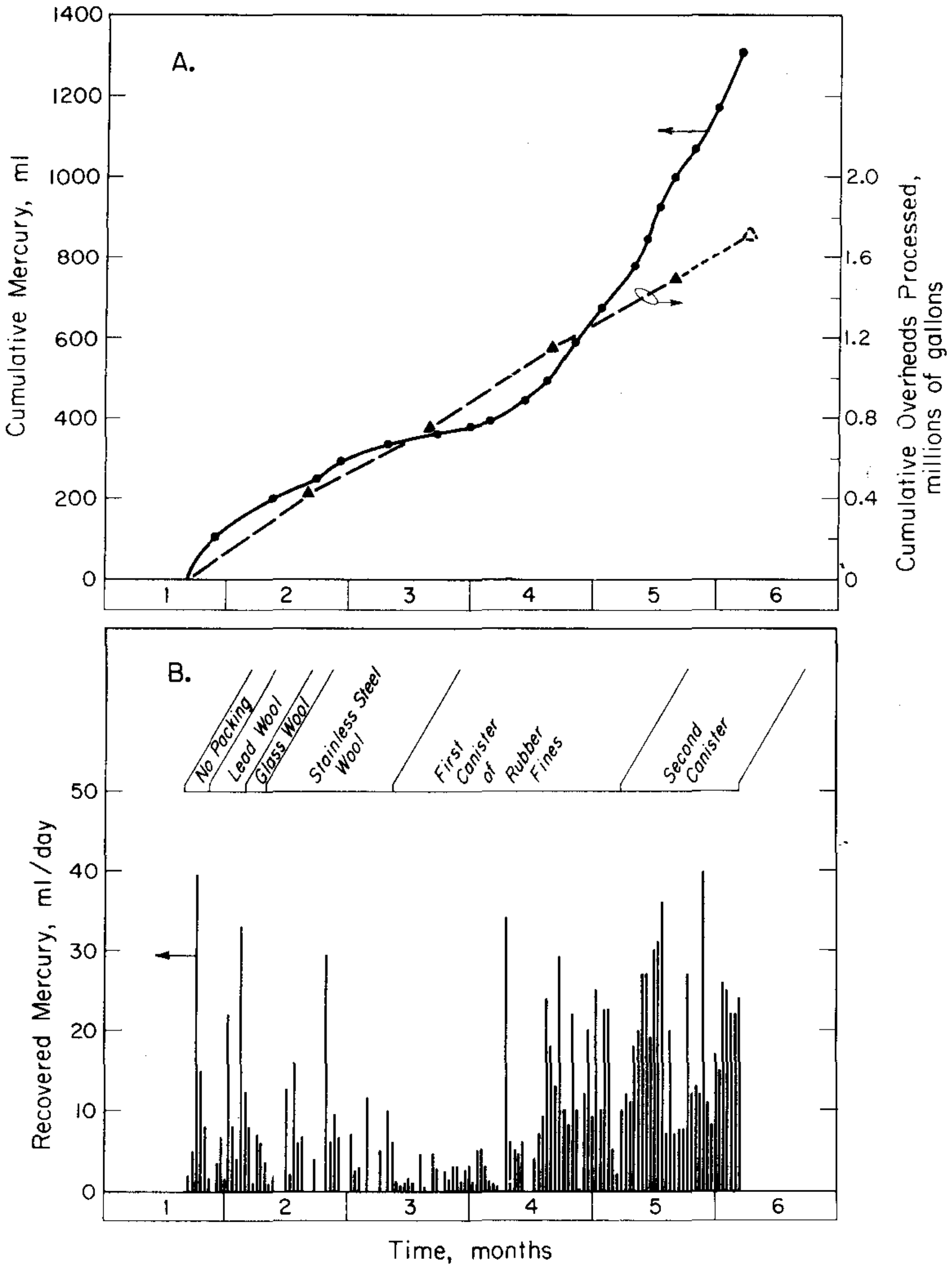

FIGURE 3. Volume of Mercury Removed by First Cyclone Separator

Although liquid mercury was collected only at the first cyclone separator, there was a visible coating of microscopic droplets of mercury on the internal surface of the second cyclone separator. To reduce this accumulation in the second separator, the removal efficiency of the first cyclone separator was increased by inserting a 6-inch length of 3/4-inch pipe inside the tangential 1-inch inlet pipe. The resulting velocity increase from 3.7 to 6.0 ft/sec raised the effective g forces in the cyclone separator by about a factor of 2.5. Pressure losses remained at less than 0.5 psi, and no further accumulation of mercury at the second cyclone separator was observed.

The amount of physically separable liquid mercury in the condensate was usually 1 to 2 ml per 1000 gallons of overheads throughput (equivalent to 3600 to 7200 ppb). The nonseparable mercury varied from 200 to 11,000 ppb, but was usually between 1000 and 2000 ppb. Thus, approximately 80% of the total mercury was removed as liquid by the first cyclone separator.

The amount of mercury in the condensate depends on the nature of the waste being evaporated. At the start of one six-month test, evaporator feed was abnormally low in dissolved solids and did not represent normal process waste. Average liquid mercury collection declined from 10 cc/day in the first week of mercury-removal column operation to about 2 cc/day in the week preceding resumption of normal feed. Mercury accumulated during this period is believed to have come from residual mercury in the evaporator. When normal feed was resumed, mercury collection rose to 15 cc/day (Figure 3).

MERCURY REMOVAL BY PACKED COLUMN

Packing material in the mercury removal column may serve a single or a dual purpose. Any fibrous packing should agglomerate fine suspended particles (that escape the first cyclone separator) to enhance removal by the second separator. The fibrous packing serves a dual purpose if it can also react chemically with mercury.

Several packing media were selected for test in the mercury removal column. Glass and stainless steel wool were tested as examples of single purpose column packings. Lead wool, used for many years in mercury traps, was selected for the dual purpose packing. In addition, recent development work at the Savannah River Laboratory has shown that finely ground vulcanized rubber could be an effective medium for chemical removal of mercury. Subsequent exploratory work showed that ground vulcanized rubber containing 1 wt % sulfur had a mercury absorption capacity of 7.5 wt %; hence, this medium was also tested.

Lead Wool

Twenty-five pounds of lead wool were placed in the mercury removal column. Three mechanisms were postulated for contributing to mercury removal by lead wool: amalgamation with impinging mercury droplets; exchange with ionic mercury, and agglomeration of particles for removal by the second cyclone separator. None of these mechanisms were valid. The overheads from the waste evaporator normally had a pH of 11.0 or greater and a temperature of 70 ±5°C. Under these conditions a fine, pale-yellow sludge formed in the effluent from the lead wool. The sludge coated all internal surfaces and was unexpectedly high in radioactivity. Analyses showed the sludge was primarily lead (>25%), but contained a substantial amount of mercury (5%).

Mercury removal by lead wool (Figure 4) was not significantly better than with the second cyclone separator alone. Also, lead was dissolved into the stream, contributing more lead to the waste effluent than the small amount of mercury that was removed. This factor alone would have eliminated lead as a candidate for this application, and the yellow sludge and radioactivity buildup were additional disadvantages.

Glass Wool and Stainless Steel Wool

A very fine, long filament form of *Pyrex** glass wool and a fine grade of stainless steel wool, relatively much coarser, were tested. The only mechanism of mercury reduction expected from these materials was agglomeration for subsequent removal by the second cyclone separator. Little or no benefit resulted from the inert packings (Figure 5).

Rubber Fines

Mercury absorption by ground vulcanized rubber was investigated in laboratory apparatus and in the condensate piping of the waste evaporator. All work was done with fresh overheads and ground rubber fines from tires containing an estimated 0.8% sulfur.[6] The mechanism of mercury absorption by the rubber has not been fully explained, but appears to involve reaction with cross-linked sulfur, which remains tightly bound to the elastomer molecules. Attempts to elute the mercury have not been effective, but destructive distillation appears promising in laboratory tests.

---

* Registered trademark of Corning Glass Works, Corning, New York.

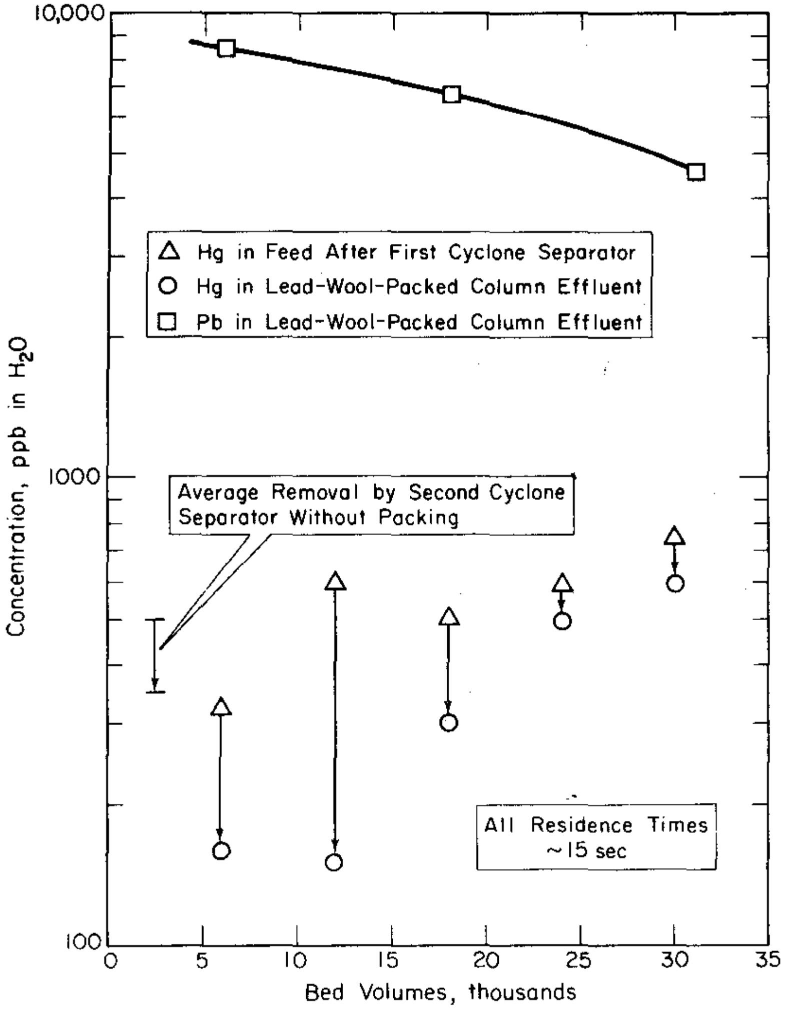

FIGURE 4. Mercury Removal by Lead-Wool-Packing

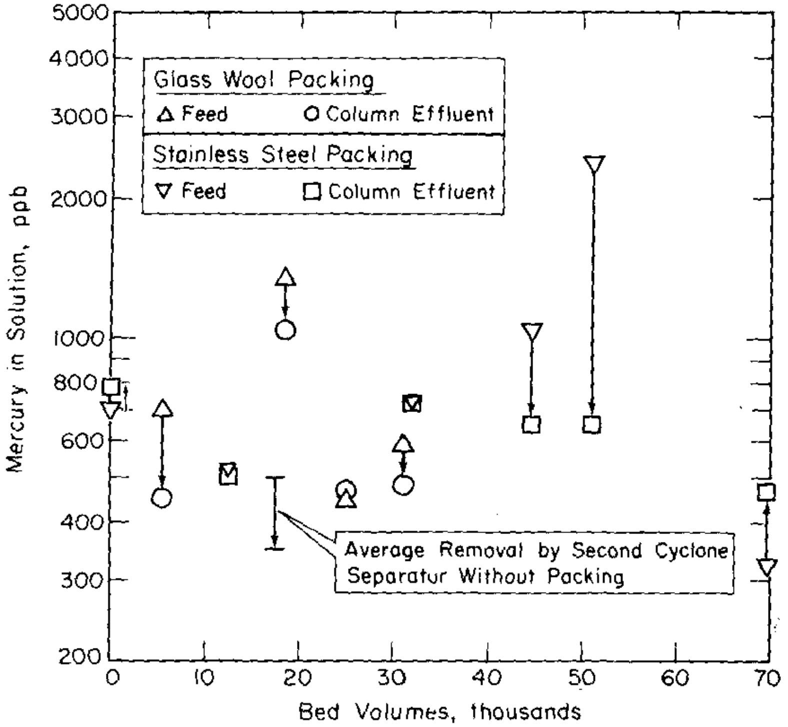

FIGURE 5. Mercury Removal by Fibrous Glass and Stainless Steel Packing

The laboratory investigations yielded three important conclusions:

1. Mercury in water can be reduced to <5 ppb by tire rubber fines (Table I).

2. Absorption rates may be affected by temperature (Table I).

3. Absorption is unaffected by pH values between 2 and 13 (Table II).

The absorption data shown in Table I were obtained by placing fresh evaporator overheads in a beaker mounted in a constant temperature bath and then adding a volumetric excess of ground rubber. At predetermined times, a screened tube was inserted into the liquid, and samples were withdrawn, thus simulating residence times in a packed bed.

TABLE I. Effects of Contact Time and Temperature on Mercury Removal by Ground Rubber (Laboratory Data)

Mercury in Solution, ppb	Contact Time with Rubber, minutes	Temp, °C	Mercury Remaining, ppb
750	5	70	< 5
750	30	70	< 5
980	5	50	15
980	10	50	8
980	30	50	< 4

TABLE II. Effect of pH at 25°C on Mercury Removal by Ground Rubber (Laboratory Data)

Solution	pH	Mercury in Solution, ppb Before	Mercury in Solution, ppb After	Time
Acidified overheads	2	750	< 5	30 minutes
Actual overheads	11	980	< 4	30 minutes
Heavy water	13	4000	180	30 minutes
		4000	2.7	2-1/2 days[a]

---

[a] Weekend; exact time was not determined.

The rubber used in the laboratory and in the mercury removal column is a normal waste product from the grinding operation performed to prepare used tires for recapping. Handling costs for procuring large quantities of this waste rubber were estimated to be one cent per pound. The very fine, near-dust portion was chosen for these tests. This material constitutes 10 to 15% of the total ground rubber and is collected in an air-solid cyclone separator which follows a gravity separator in the tire recapper's vacuum-operated dust collection system. Coarse ground rubber from the gravity separator was also tested, but it only reduced mercury to 10 ppb under the same conditions that the finer material reduced the mercury to <4 ppb.

Plant tests with finely ground rubber were made with a replaceable canister inserted in the original mercury removal column, and with a 10-foot-long column made of 2-inch pipe. In the former, 6.5 pounds of rubber was loaded into the separable 1.9-gallon canister. The second (upper) cyclone separator, already shown to be unnecessary, was removed to provide more space for the canister (Figure 6).

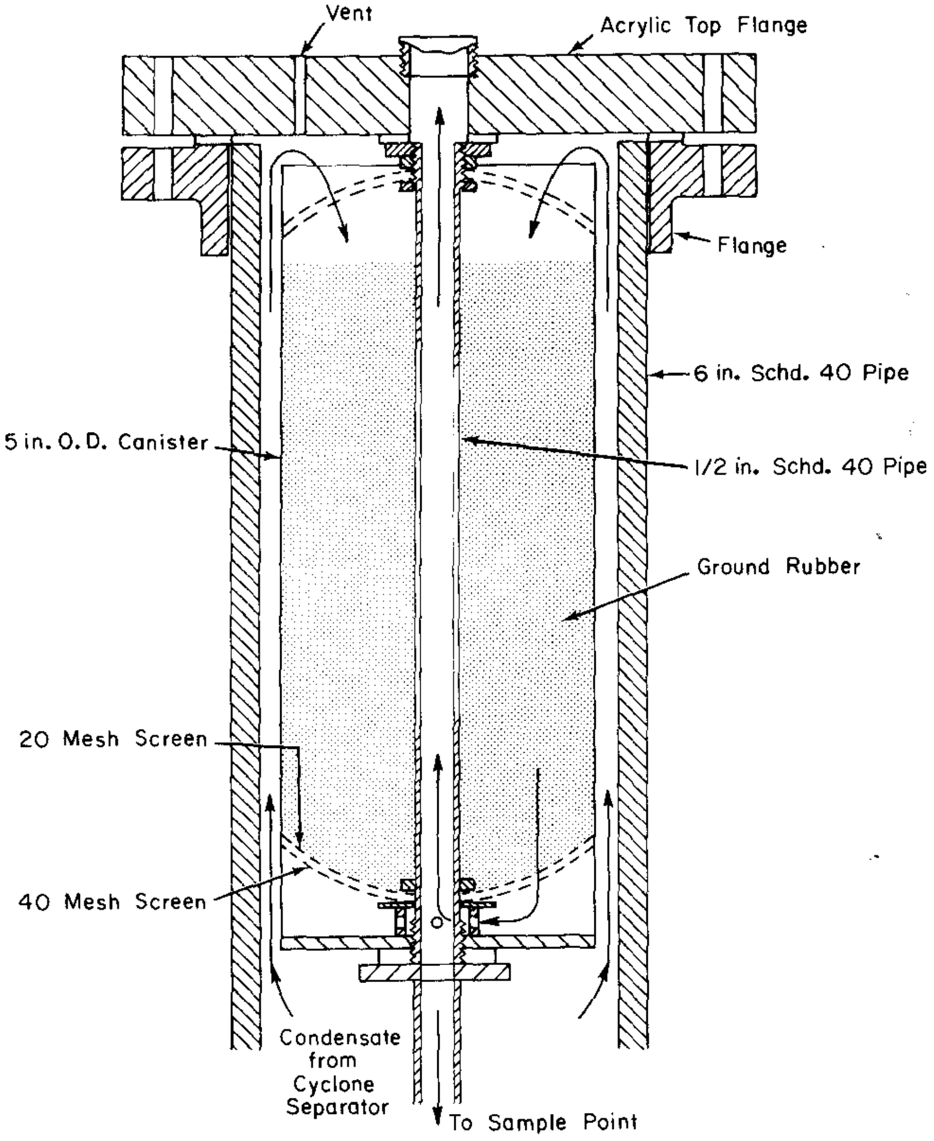

FIGURE 6. Canister for Ground Rubber in Downflow Mode

After 20, 3000, and 6000 bed volumes had been processed by the canister in the mercury removal column, flow rate was varied to determine the effect of residence time and other variables (Figure 7). The inflection in the 3000-bed-volume curve is attributed to the mass flow rate falling below the 1 gpm/ft^2 generally cited as a minimum for packed beds. Similar, but different, data involving bed volumes processed are shown on Figure 8.

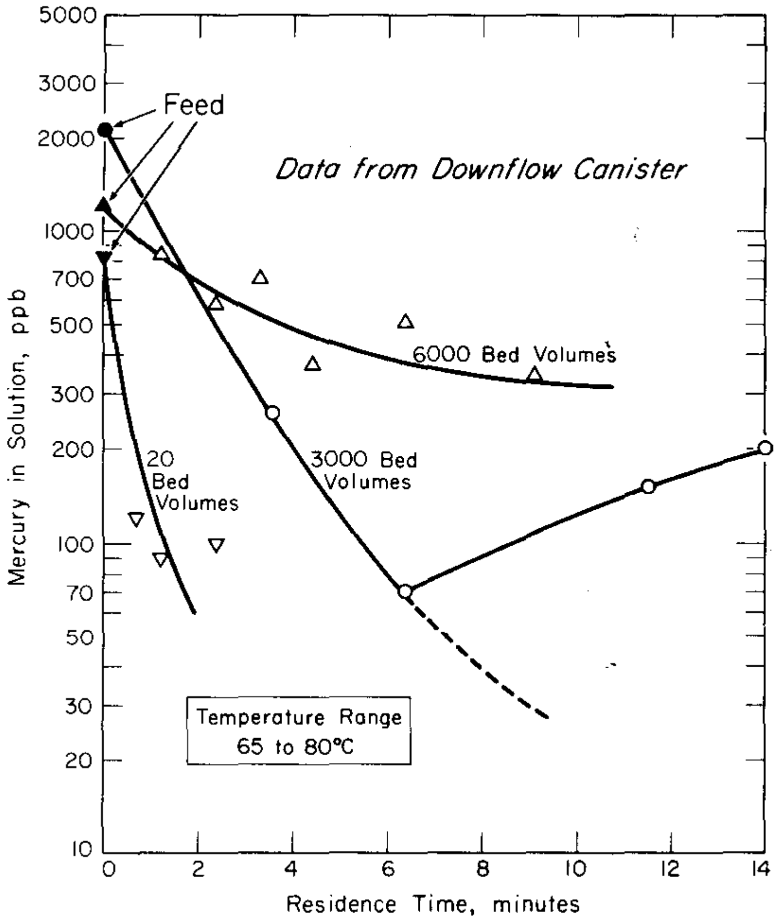

FIGURE 7. Effect of Residence Time on Mercury Absorption by Rubber

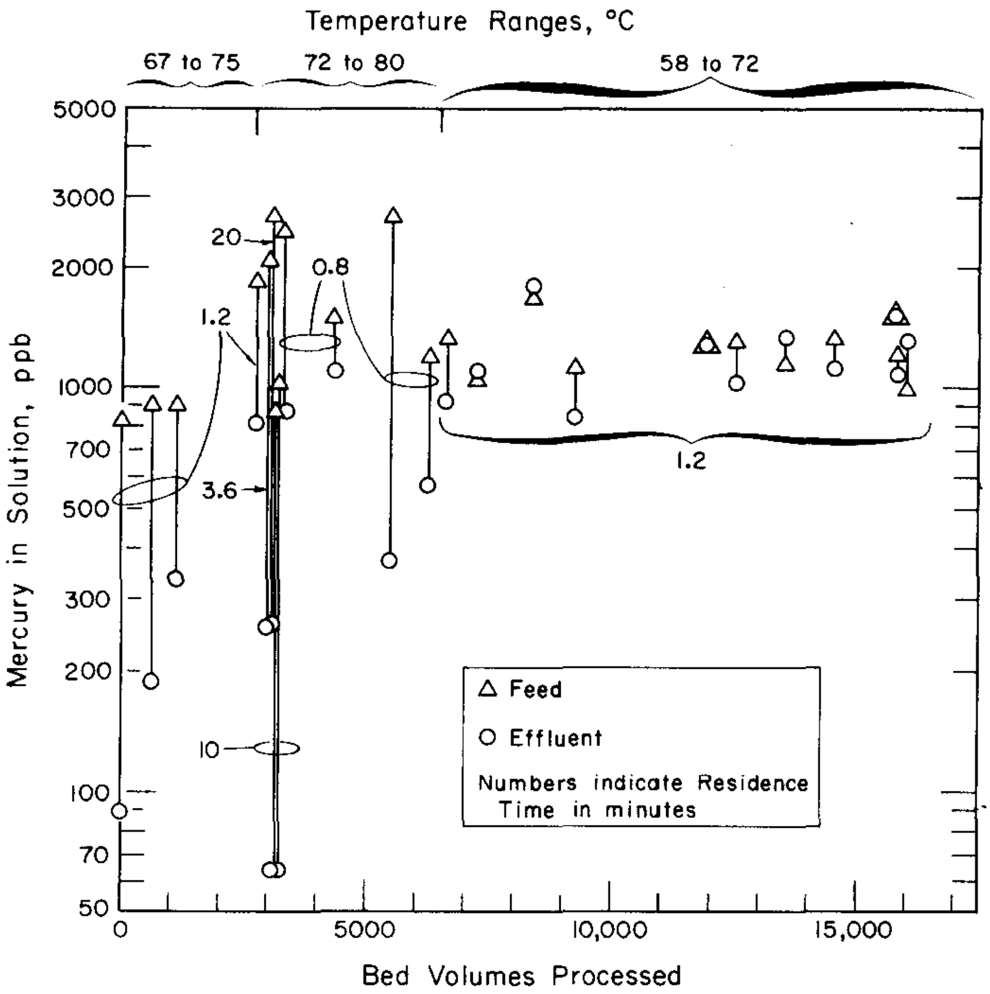

FIGURE 8. Mercury Absorption by Rubber in Downflow Canister

When the canister was disassembled, the top of the rubber bed had a light, silver-gray coating of small non-coalescing droplets of mercury that had been trapped or filtered by the rubber (Figure 9). The droplets ranged in size from 4 to 70 μm and are strong evidence that the rubber bed functions quite well as a filter.

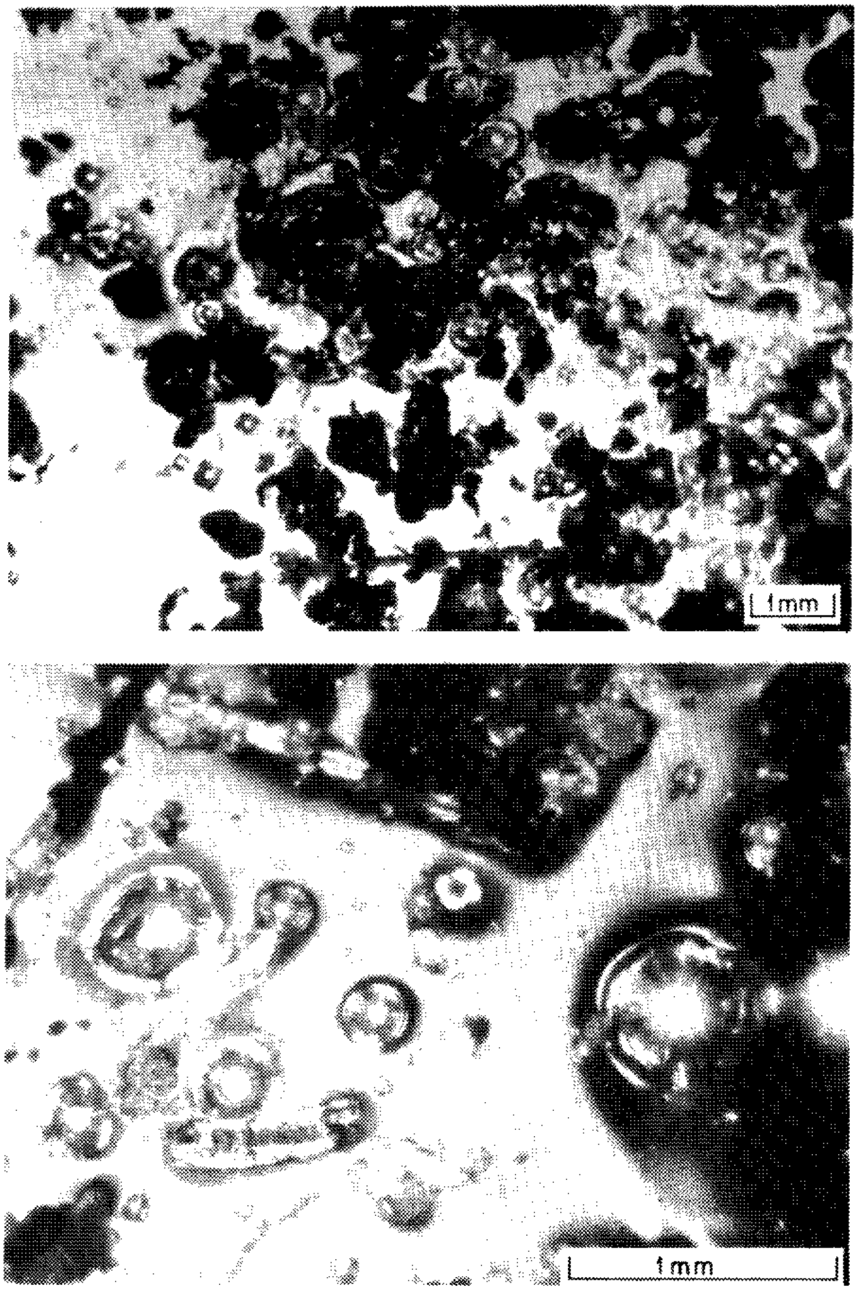

FIGURE 9. Mercury Droplets on Rubber Fines

The residence times and superficial velocities suggested by data from the short-column canister runs were tested in a 10-foot-long pilot column (Figure 10). The pilot column was packed with about six pounds of rubber that had been pre-wetted in a separate container with water containing a small amount of detergent. Wetting was found necessary when loading the long column to avoid gross amounts of trapped air and resultant high pressure losses through the rubber bed. Only particles wetted enough to sink in the wetting bucket were slurried into the column.

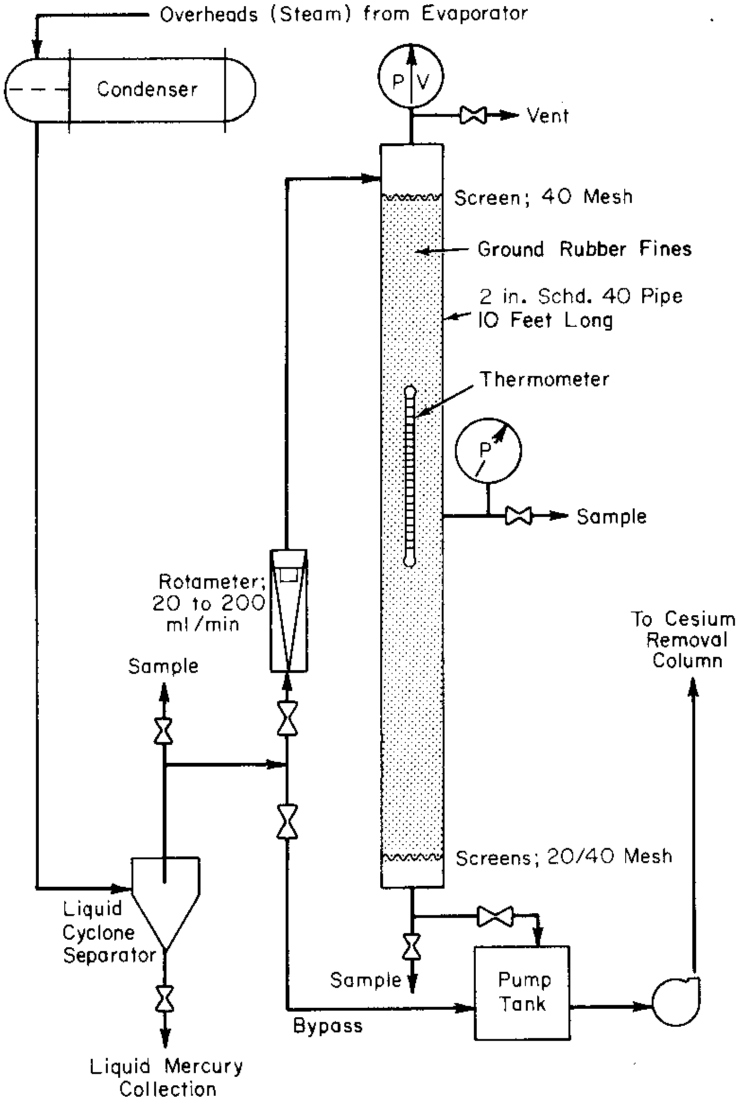

FIGURE 10. Flow Diagram for Pilot-Scale Mercury Removal Column

Much cleaner effluents were produced by the pilot column than by the canister tests (Figure 11), but the service life was only about one-fifth of the 3000-bed volume throughput predicted from the canister data. For the first 170 bed volumes, effluents were less than 10 ppb mercury, with some results being as low as 5 or 6 ppb. Acceptable results of 100 ppb were achieved for about 650 bed volumes. The reason for the shorter bed life was not investigated.

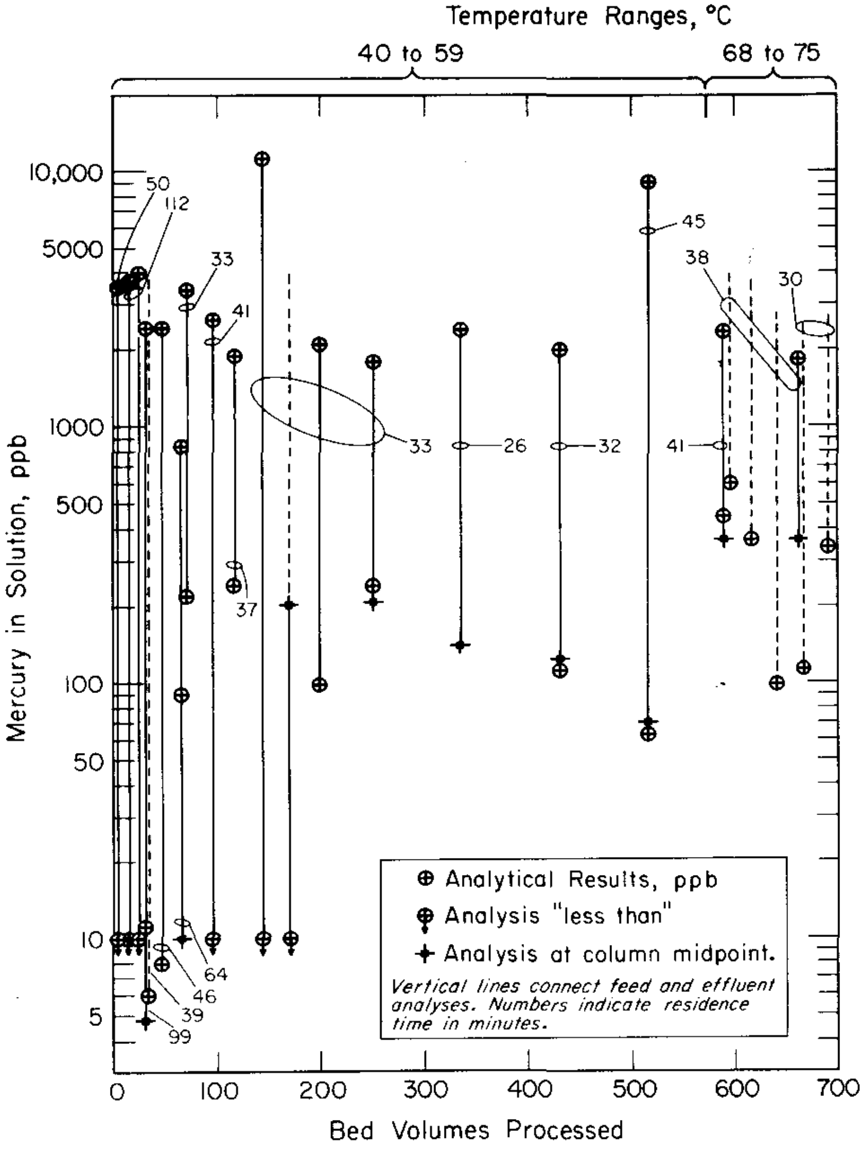

FIGURE 11. Mercury Absorption by Rubber in Pilot-Scale Column

SUGGESTED FUTURE WORK

Since improved mechanical removal of elemental mercury would extend the service life of any packing media for removing mercury by chemical means, improvements in mechanical separatory devices should be investigated. Tests made on unacidified overheads allowed to cool and settle overnight showed that the mercury concentration decreased from 1000 ppb to 150-200 ppb. However, cooling of the overhead stream that passed through a low-point gravity collector showed no change in performance of the collector; hence, delay (time to settle) may have been the contributing factor in the above tests.

The present work is adequate to establish the design basis for a full-scale prototype. Ideally, such a prototype would be instrumented to determine heat loss, pressure drop, compressibility, and service life of large, rubber-packed beds and should lead to an optimum design applicable over a broad range of conditions.

ACKNOWLEDGMENTS

The writer gratefully acknowledges the substantial contributions to this work by personnel of the Savannah River Laboratory: E. L. Albenesius, for the original idea for extracting mercury from waste streams with ground vulcanized rubber; E. R. Russell, for the exploratory laboratory work; and R. W. Taylor, for the photomicroscopy work. G. D. Osbon of Osbon Auto Supply, Augusta, Georgia, provided the test quantities of ground rubber.

REFERENCES

1. H. B. Weiser. *Inorganic Colloids,* Volume 1, John Wiley & Son, New York (1933).

2. "Sharing the Secrets." *Chem. Week,* p. 16 (July 14, 1971).

3. "Paring Mercury Pollution." *Chem. Eng.,* p. 70 (Feb. 22, 1971).

4. "Process Removes Mercury in Plant Wastes." *Chem. Eng. News,* p. 48 (Dec. 14, 1970).

5. "Winning Heavy Metals from Waste Streams." *Chem. Eng.,* p. 62 (April 19, 1971).

6. D. V. Sarbach, R. W. Hallman, and W. E. Moles. *Rubber Age,* p. 47 (August 1970).