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REMOVING RADIOSTRONTIUM FROM MILK—CURRENT STATUS OF A PILOT PLANT PROCESS

Strontium^{90}—the long-lasting contaminant that results from fallout—can be removed from milk. A tentative process for removing it has been developed to the pilot-plant stage. The work is the result of a cooperative project by the Public Health Service of the Department of Health, Education, and Welfare, the Agricultural Research Service of the U. S. Department of Agriculture, and the U. S. Atomic Energy Commission. The pilot plant has been set up in Beltsville, Maryland, at the Dairy Products Laboratory of the ARS Eastern Utilization Research and Development Division. The present installation is the result of over 2 yr of research at this laboratory (2, 3) and at the Robert A. Taft Sanitary Engineering Center of the Public Health Service in Cincinnati, Ohio (5). The process is based on evidence presented earlier by the University of Tennessee (1) and the Canada Department of Agriculture (4) that strontium^{90} could be removed from milk by an ion-exchange process.

Research with this pilot plant indicates that the process could be adopted commercially in the event that radiostrontium in milk should reach dangerous levels. However, study of engineering problems and further research to establish the most economical procedure are needed before the fluid milk supply of the United States could be treated expeditiously, if such treatment should ever become necessary. This report is not intended to encourage premature entrance into this technical field by the dairy industry; it is presented only as an interim report to acquaint the dairy industry with the present status of the research.

PRINCIPLE OF THE PROCESS

The process is based on the ion-exchange principle. Milk contaminated with radiostrontium is passed through a bed of synthetic resin charged with a mixed solution of metallic ions—calcium, potassium, sodium, and magnesium—which are present in milk. As the milk passes through the column, the strontium ions in the milk change places with the metallic ions on the resin.

An important feature of the process is that the acidity of the milk is adjusted, before passing it through the resin column, from its normal pH of 6.6 down to 5.3 or 5.4. At the normal pH of milk, most of the strontium is bound by other milk constituents and is slow to be exchanged. Passing 25 resin bed volumes of milk at normal pH through the column removes an average of less than 50% of its strontium. At the low pH, strontium is largely converted to a soluble and more readily exchangeable form.

EFFECTIVENESS AND ESTIMATED COST OF PROCESS

With this pilot-plant process, about 90% of the radioactive strontium in milk can be removed. The process has been developed to secure maximum removal of strontium^{90}, inducing only a minimum of adverse changes in the milk's chemical composition, physical stability, or flavor. The appearance of the treated product is normal after homogenization and pasteurization. Flavor scores of the treated milks, as judged by an expert panel, compare favorably with the control samples. They usually average about 1.0 point below the controls on the A.D.S.A. score card. Procedures for minimizing changes in the composition of the major cations in milk have been worked out. Studies on nutritional changes as a result of the ion exchange treatment are in progress.

The cost of materials used for this process is primarily that of the salts used to regenerate the columns after they become exhausted (i.e., when the amount of strontium^{90} removed falls to some predetermined level). The cost of these salts, plus that of the citric acid and potassium hydroxide used to adjust and then restore the milk's normal pH, is estimated at about 2¢ per quart of milk processed. This estimate is based on a process which reuses the salt solutions so that maximum efficiency is obtained, and on the use of USP grades of salts. If the regenerating solution is not recovered, the cost may be as high as 5¢ per quart. Since the salts used for regeneration are not a direct addition, investigation is now under way to determine whether less expensive grades may be suitable.

The efficiency of this process is closely related to the amount of milk that can be passed through a column before the column becomes exhausted. This depends on a predetermined level of strontium removal. It can be considered acceptable if 25 resin bed volumes of milk can be processed before a column must be regenerated.

PRESENT PILOT-PLANT EQUIPMENT

The accompanying figure shows schematically the operations involved in the process. There are two glass ion-exchange columns, 5 ft long and 6 inches in diameter. They are fitted with sufficient valves for directing the milk and the necessary solutions through the resin bed in controlled sequence for a continuous operation.

While milk is flowing through one column, the other is being cleaned and regenerated for reuse. The drawing depicts a batchwise method for adjusting the milk's acidity with citric acid. On a large scale this solution could be added with a metering pump to a continuous flow of milk, as is shown for neutralization with potassium hydroxide.

These pilot-plant facilities were designed for a capacity of about 100 gal per hour. The columns contain about two-thirds of a cubic foot of resin. This allows for sufficient head space for upflow washings.

STEPS IN THE PROCESS

The process for removal of radiostrontium from milk includes the following operations:

1. *Charging the resin bed.* The resin bed is charged with a mixed salt solution containing the chlorides of calcium, potassium, sodium, and magnesium. The quantities of each are selected so that the resin will be equilibrated with the proper ratio of cations. Thus, a minimum change in the composition of the milk is assured when it is passed through the resin. The composition of the salt solution found suitable for this operation is as follows (in grams per liter of solution):

Calcium chloride ($CaCl_2 \cdot 2\ H_2O$)	53.5
Potassium chloride	23.1
Sodium chloride	8.5
Magnesium chloride ($MgCl_2 \cdot 6\ H_2O$)	15.1

2. *Acidification of the milk.* Cold, raw whole milk is adjusted to a pH of 5.3-5.4 with 0.75 molar citric acid. The acid is added slowly and with thorough mixing. About 7% more strontium could be removed if the pH of the milk were lowered to 5.2 instead of 5.4. But at this acidity, laboratory experience has shown a greater likelihood of protein precipitation. This may require excessive pressure in the resin column to keep the milk flowing. At pH 5.4, milk temperatures from 40 to 80 F have been found to have no effect on the amount of strontium removed. Temperatures above 80 F cannot be used as the milk is sensitive to coagulation at low pH.

3. *Putting the milk through the column.* The acidified milk is filtered and pumped downflow through a column of cationic ion-exchange resin at a rate of about 2.5 gal per minute per cubic foot of resin. The resin should be of the nuclear sulfonic acid type, such as Amberlite IR-120 or Dowex 50W.[1] A small positive pressure of 2 psi or greater is usually required to maintain a constant flow rate through the column. Too fast a flow rate should be avoided, since the amount of strontium removed decreases with increasing flow rate. A drop of 8 to 10% can result from increasing the rate from 0.25 to 0.5 resin bed volume per minute.

4. *Neutralizing the milk.* The effluent milk is collected in a surge tank, where it is readjusted to normal pH by adding dilute potassium hydroxide or a mixed solution of sodium and potassium hydroxide. If the milk is neutralized entirely with sodium hydroxide, it acquires a salty flavor.

5. *Processing the treated milk.* After neutralization, the milk is pasteurized, homogenized, and deodorized to remove the water added in the acidification and neutralization steps.

6. *Cleaning and sanitizing the resin.* As the resin in one column becomes exhausted, milk flow is diverted to another column, while the first is being cleaned. This is done by rinsing with warm water, followed by an upflow wash with a nonionic cleaning solution at 140 to 160 F. The resin may then be sanitized with hypochlorites at a chlorine concentration of about 50 ppm. Sanitizing is not necessary with every cleaning, but it may be desirable at the end of each day's run or if the resin is idle for a considerable period. Another means of controlling bacterial growth is through the use of heat, since the resins will withstand temperatures up to the boiling point of water. Washing or sanitizing solutions are immediately followed by rinse water.

7. *Regeneration of the resin.* The clean resin is then regenerated with a mixed salt solution of the same composition as that used to charge it initially (Step 1). When applied to a resin column that has been in use for the processing of contaminated milk, the salt solution simultaneously strips the radiostrontium from the resin and regenerates the resin for the next cycle. Essentially 1.0 volume of salt solution is required per volume of milk processed. Most of this quantity may be recovered and used again. In this case from ¼ to ⅓ of the stripping solution would be discarded and replenished with fresh solution after each cycle. When excess salts have been removed with a water rinse, the column is ready for another milk cycle of 25 bed volumes.

RESEARCH STATUS OF THE PROCESS

A great deal of research has been required to bring this process to its present state of

[1] The use of trade names is for the purpose of identification only, and does not imply endorsement of the product or its manufacturer by the U. S. Department of Agriculture.

development. Much more is still to be done to improve the method, to assure a nutritionally satisfactory product, to evaluate possible sanitation problems, and to reduce its cost. The current research status of the process can be summarized briefly by mentioning the work done in establishing operating conditions for the equipment and then in evaluating the efficiency of the pilot-plant process by actual use with milk intentionally contaminated with known amounts of radiostrontium.

Establishment of operating conditions. The process described above was arrived at through a careful study of the ion-exchange principle of removing radiostrontium from milk. Several different types of resins have been evaluated for their effectiveness. Some basic research has been done in the area involving cationic equilibria of resin-milk systems and resin-salt solution systems. This work was necessary to develop optimum procedures for cleaning the resin, removing strontium^{90} from the exhausted resin, and regenerating the resin for reuse. Work has also been in progress on the nature of the strontium complexes in the milk. Such basic information should aid in explaining the results obtained and may lead to further improvements in the process.

Work in progress designed to further reduce the cost of the process is primarily concerned with the salts used to regenerate the resin. Techniques for using reverse flow regeneration may reduce slightly the quantity of salts required. Studies on reclaiming a portion of the regenerating salts are being continued.

Production of contaminated milk for evaluation of the process. The pilot-plant has been used experimentally in the processing of milk obtained from a cow fed measured doses of radiostrontium. Because quick analysis of the strontium content of the milk samples before and after processing was essential to an accurate evaluation of the process, the cow is fed strontium^{85} rather than strontium^{90}. Unlike strontium^{90}, which requires a long and tedious procedure for analysis, strontium^{85} is a gamma-emitting radionuclide that can be assayed with a minimum of sample preparation.

Strontium^{85} is fed to a Holstein cow either orally or intravenously to obtain levels in the milk of about 1 μc per quart. This is a much heavier concentration of radiostrontium than has been found to occur in fallout, where levels of the order of 10 $\mu\mu$c of strontium^{90} per quart have been detected. The higher levels for this research have been necessary for rapid assay of a large number of samples. Since both levels represent much smaller weights of radiostrontium than the stable strontium in milk, the amount removed by an exchange process should be the same on a percentage basis. This has been confirmed by preliminary work with levels of about 200 $\mu\mu$c per quart.

Work is now in progress at this laboratory to apply the techniques to the removal of environmental levels of strontium^{90}.

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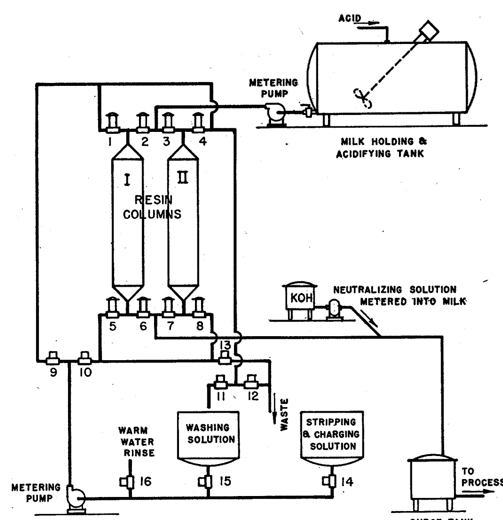

FIG. 1. Flow diagram showing strontium^{90} removal by ion exchange resin.

FIGURE KEY

Flow Operation of Equipment with Milk Flowing Down Column I and Regeneration Process for Column II.

A. Valves No. 2 and No. 6 are opened for 60 min, allowing raw milk to flow down Column I. At the same time that the milk is flowing through Column I, Column II is being regenerated in sequence as follows:

B. Valves No. 16, 9, 4, 8, and 13 are opened from 2-4 min, allowing warm rinse water to flow down Column II.

C. Valves No. 15, 10, 8, 4, and 11 are opened for 8 min, allowing washing solution to flow up Column II.

D. Valves No. 16, 9, 4, 8, and 13 are opened from 2-4 min, allowing rinse water to flow down Column II.

E. Valves No. 14, 9, 4, 8, and 13 are opened for 25 min, allowing stripping and charging solution to flow down Column II.

F. Valves No. 16, 9, 1, 5, and 13 are opened from 2-4 min, allowing rinse water to flow down Column II until chloride-free.

Flow Operation of Equipment with Milk Flowing Down Column II and Regeneration Process for Column I.

A. Valves No. 3 and 7 are opened for 60 min, allowing raw milk to flow down Column II. At the same time that the milk is flowing down Column II, Column I is being regenerated in sequence as follows:

B. Valves No. 16, 9, 1, 5, and 13 are opened from 2-4 min, allowing warm rinse water to flow down Column I.

C. Valves No. 15, 10, 5, 1, and 11 are opened for 8 min, allowing washing solution to flow up Column I.

D. Valves No. 16, 9, 1, 5, and 13 are opened from 2-4 min, allowing rinse water to flow down Column I.

E. Valves No. 14, 9, 1, 5, and 13 are opened for 25 min, allowing stripping and charging solution to flow down Column I.

F. Valves No. 16, 9, 1, 5, and 13 are opened from 2-4 min, allowing rinse water to flow down Column I until chloride-free.

Notes:

All valves are normally closed and only opened as indicated.

The flow rate of the milk pump is 96 gal per hour.

The flow rate of the regeneration pump is 6 gal per min.