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Effect of Calcium Removal by Ion Exchange on the Properties of Fluid Milk[a,b]

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High temperature heat treatment of milk to increase resistance to lipid oxidation is a commercial practice in the manufacture of dry whole milk and other dairy products. Denaturation of serum proteins and lowered dispersibility of casein are often undesirable resultants of this treatment. Evidence exists that partial removal of calcium from milk increases the resistance of proteins to heat-induced changes. This paper describes the use of synthetic resinous ion exchangers in the removal of calcium from milk. A larger portion of calcium may be removed from milk with less change in sensory rating by the use of anionic and cationic resins in intimate mixture than by the use of these resins singly or in series.

At present, high temperature preheating of milk in the manufacture of dry whole milk is commercially practiced. The increased resistance of the milk lipids to oxidation resulting from preheat treatment is thought to be due to antioxygenic sulfhydryl compounds liberated principally from the serum protein fraction of the milk *(15, 6)*. Although advantageous from the standpoint of lipid stabilization, high temperature preheating may result in certain undesirable changes, among which is the effect on milk proteins, the denaturation of serum proteins, and the destabilization of casein rendering it less dispersible and therefore the dry milk less "soluble." Thus initiated, a continuing loss in solubility during storage may result *(12)*. The effect of heat treatment on milk proteins has been discussed in a recent review *(1)*.

A characteristic tactual defect often noted in reconstituted dry milk and in evaporated milk described as "rough," "chalky," or "astringent" is said to be the result of heat-induced denaturation of serum proteins *(7)*. The importance of salt composition in the heat coagulation of fresh and evaporated milk was first discussed by Sommer and Hart *(14)*. As related to heat coagulation, calcium appears to be the controlling ion in the salt system of milk *(4)*. An excess of calcium increases the instability of milk proteins during heat processing.

Although it has been a commercial practice for many years to increase the heat stability of evaporated milk by binding excess calcium with such added salts as sodium citrate or disodium phosphate, it is only since the work of Lyman *(11)* in 1933 that ion-exchange materials have been used to modify the mineral constituents of milk, chiefly to decrease calcium. Varied application of the exchange procedure has since been reported. A frozen milk of normal flavor and with improved physical stability has been obtained by removal of as little as 10-15% of the calcium *(5)*. Other workers have reported, however, that although a retarding effect on casein flocculation in frozen milk products is accomplished by calcium removal, using a cationic exchange procedure, an adverse effect on flavor appears to limit the utility of such treatment *(16)*. Ion exchanged milk added as a fluid, powder, or concentrate to evaporated milk was found capable of stabilizing the product against coagulation during sterilization *(8)*. Powdered cream readily reliquefiable and stable to heat coagulation has been produced by ion-exchange treatment to lower the calcium content before drying *(2)*. Ion exchange has also been used to convert insoluble acid caseinate into a soluble alkali-metal caseinate of reduced ash content *(2)* and to produce smoother ice cream *(3)*. The theory and general application of ion exchange has been reviewed recently by Kunin *(9)*, Kunin and Myers *(10)*, and Nachod *(13)*.

EXPERIMENTAL

The principal objective of the work here described was to determine, preliminary to heat treatment studies and spray drying, the maximum extent of demineralization (specifically, calcium removal) of fluid milk, using synthetic ion exchange resins, consistent with a high sensory evaluation of the treated milk.

Resinous cation exchangers were employed in this study either in the hydrogen cycle, i.e., the resins were regenerated to contain exchangeable hydrogen ions, or in the sodium cycle, i.e., the resins were regenerated to contain exchangeable sodium ions. The resinous anion exchangers, used in conjunction with the hydrogen form of the cation exchanger to remove by adsorption acids formed in cationic exchange, were regenerated with sodium or ammonium hydroxide.

The ion exchange process was conducted in two ways: (a) by batch operation and (b) by column operation.

A mixed-bed procedure recently introduced[d] is a column procedure employing an intimate mixture of cationic and anionic exchange resins in a single bed.

As applied to milk, the mixed-bed procedure offers definite advantage over the procedures described previously. By the use of a mixture of a weakly acidic cationic resin and a weakly basic anionic resin the demineralization is controlled within a relatively narrow range of pH about neutrality. The procedure for mixed-bed demineralization as used in this study is described later in some detail.

[a] This paper reports research undertaken at the Quartermaster Food and Container Institute for the Armed Forces, and has been assigned number 444 in the series of papers approved for publication. The view or conclusions contained in this report are those of the authors. They are not to be construed as necessarily reflecting the views or indorsement of the Department of Defense.

[b] Presented at the Thirteenth Annual Meeting of the Institute of Food Technologists, Boston, Massachusetts, June 23, 1953.

[c] A field installation of the Research and Development Command, Office of the Quartermaster General.

[d] Termed *Monobed* by the Resinous Products Division, Rohm and Haas Co. See *Amberlite Monobed Deionization*, Rohm and Haas Co., page 8.

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TABLE 1

Ion exchange resins used in the demineralization of milk

Resin	Amberlite IR-100	Amberlite IRC-50	Amberlite IR-120	Amberlite IR-4B	Amberlite IRA-400	Amberlite IR-45
Exchanger type	Cation	Cation	Cation	Anion	Anion	Anion
Active group	Sulfonic	Carboxylic	Sulfonic	Modified amine	Modified amine	Modified amine
Behavior	Strongly acidic	Weakly basic	Strongly acidic	Weakly basic	Strongly basic	Weakly basic

The synthetic resinous exchangers used were commercial products designated as Amberlites. Table 1 lists the types of resins used.

Use of cationic exchange resins by the batch technique. The cationic exchange resin, Amberlite IR-100, in the acid cycle (IR-100-H) was added with agitation to aliquots of homogenized whole milk in amounts sufficient to result in a series with decreasing calcium values. The milk was separated from the resin by decantation and filtered through cheese cloth.

This procedure was repeated with other aliquots of untreated milk except that the sodium form of the cationic resin (IR-100-Na) was used subsequent to the acid form to readjust the pH of the milks to the initial value. The combination of resins was also employed in the reverse order.

The resin-treated samples were judged by a 17-member milk panel using a 9-point quality rating scale in which: 9 was *excellent;* 8, *very good;* 7, *good;* 6, *below good but above fair;* 4, *below fair but above poor;* 3, *poor;* 2, *very poor;* and 1, *extremely poor.* Results obtained (Table 2) are plotted as a function of calcium content in Figure 1.

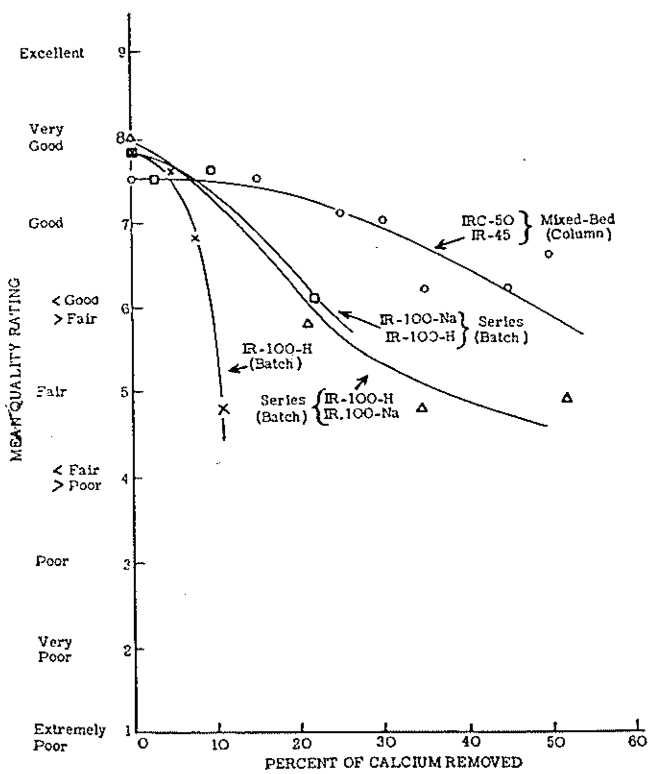

Figure 1. Quality ratings for batch-treated and mixed-bed demineralized whole milk.

From sensory considerations, the factors limiting extent of exchange were the resultant acidity when the resin was used in the hydrogen cycle and resultant saltiness where the resin was used in the sodium cycle or where the resin was employed in both cycles in sequence. Thus, by the use of the cationic exchanger in the hydrogen cycle demineralization equivalent to approximately 10% calcium removal with only slight changes in sensory evaluation was obtained whereas only slight flavor changes were produced by removal of approximately 20% calcium using both forms of the resin in series.

Theoretically, it appeared that further calcium removal without an appreciably lowered sensory score could have been accomplished through the use of a cation exchanger in the hydrogen cycle followed by an acid adsorbing resin (anionic exchanger); however, in practice, this was not possible due to the low efficiency of the latter in milk as seen below.

TABLE 2

Effects of various cationic batch exchange treatments of fluid whole milk on extent of calcium removal and milk panel rating

pH				% Calcium removed	Mean panel rating[1]
Initial	After IR-100-H	After IR-100-Na	After IR-100-H		
6.7	6.4			4	
6.7	6.2			7	
6.7	5.8			14	
6.7	5.5			18	
6.7		6.8		2	
6.7		6.9		5	
6.7		7.0		10	
6.7		7.5		18	
6.7		8.3		32	
6.7		9.3		41	
6.6				0	7.8
6.6	6.3			5	7.6
6.6	6.2			7	6.8
6.6	5.9			11	4.8
6.6		6.7	6.5	3	7.5
6.6		6.7	6.6	9	7.6
6.6		6.9	6.6	22	6.1
6.7				0	8.0
6.7	6.3	6.6		21	5.8
6.7	6.2	6.6		35	4.8
6.7	5.9	6.6		52	4.9
6.7	6.0	6.4		91	3.2

[1] Using a 9-point rating scale where 9 is *excellent* and 1 is *extremely poor.*

Use of cationic and anionic exchange resins by the batch technique. Homogenized whole milk was stirred with IR-100-H, separated by decantation and filtered through cheese cloth and aliquots were then stirred with the anionic resins IR-4B or IRA-400 until the pH remained constant and the milks were again separated.

As seen in Table 3, neither of the anionic resins, although employed in large amounts, removed the acidity resulting from cationic exchange.

TABLE 3

Effect of batchwise use of cationic and anionic resins in series on pH and extent of calcium removal from fluid milk

pH				Total calcium removed (%)
Initial	IR-100-H	IR-4B	IRA-400	
6.5	6.1	6.2		12
6.5	6.1		6.1	11

Phosphate buffered and unbuffered acidic solutions (HCl) containing either calcium chloride or casein or a mixture of the two were batch-treated with the acid adsorbing resin, IR-4B. The concentration of calcium, casein, and phosphorus of buffered solutions approximated their concentration in fluid milk. Calcium chloride alone did not affect the ability of IR-4B to adsorb acid. Both the buffer ($KH_2PO_4 \pm Na_2HPO_4$) and casein considerably increased the weight of resin required to effect a pH change. In the presence of casein and/or buffer the activity of IR-4B was so reduced as to be negligible even though large amounts of resin were used.

Use of cationic and anionic exchange resins by the mixed-bed column technique. A recent exchange technique involving an intimate mixture of an anion and cation exchanger appeared to offer advantages, cited earlier, over the two cycle systems.

The general mixed-bed procedure used in this study is described in some detail.

The ion exchange column consisted of a Pyrex glass tube 48 inches long and 1.5 inches in diameter having a drawn tip at one end. The column was charged as shown in Figure 2 with a

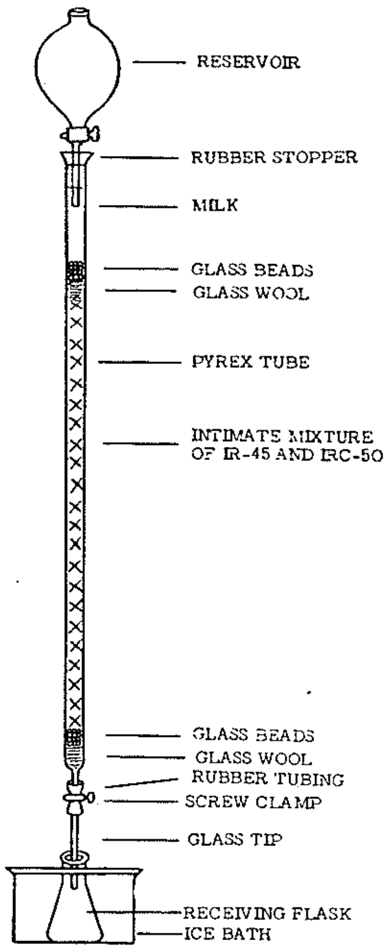

Figure 2. Ion exchange column.

mixture of equal volumes of Amberlites IR-45 and IRC-50.[e, f]

Glass wool was placed at the bottom of the exchange column to form a mat approximately one inch in depth. Above this, glass beads of approximately 5 mm. diameter were placed to a depth of one inch. The column was charged with 600 ml. (wet volume) of a mixture of equal volumes[g] of "Amberlites" IR-45 and IRC-50 in the following manner: the lower clamp was closed and approximately 50 ml. of distilled water placed in the column; the mixing rod[h] was placed in the column spiral, tip down, the mixed resins placed in the column in increments of approximately 200 ml. with vertical agitation by the mixing rod. The purpose of the water was to allow the resin to settle in a manner which avoided air pockets and channeling. The mixing rod was removed and after the resin mixture had settled the water was drained to a level approximately one inch above the resin. Glass wool to form a mat approximately one inch in depth was next inserted above the resin bed and above the mat were placed glass beads to a depth of one inch to anchor the mat. The reservoir was then attached at the top by means of a rubber stopper.

Milk was passed downflow through the column at the rate of 10 ml. per minute. A column of milk above the resin bed was maintained at a height sufficient to permit a controlled rate of flow throughout the demineralization. The temperature of the influent milk was 5-10° C. The effluent milk was collected in a flask held in an ice bath. The first liter of effluent collected, containing displaced water from the column, was discarded.

The treated milk of reduced calcium content was combined and mixed with untreated milk to give milk of any desired calcium content.

After the resin-treated milk had been collected, hot tap water was passed rapidly downflow through the column until no turbidity was evident in the effluent. The resin bed was then transferred to a tall cylinder and backwashed by introducing hot tap water upflow from the bottom of the column at a rate which resulted in a separation of the 2 resins. The water pressure was increased causing the less dense IR-45 to rise and spill over into a collecting pan while the more dense IRC-50 remained. The IR-45 was transferred to a cylinder and both resins thoroughly backwashed with hot tap water. Each of the resins was then transferred to an exchange-type column and regenerated downflow: IRC-50 using 6% HCl, IR-45 using 6% NH_4OH, both using one liter of regenerant per 300 ml. (wet volume) of resin. Each resin was then washed downflow with deionized water until the pH of the effluent wash became constant.

EVALUATION OF MIXED-BED COLUMN METHOD

Both whole and non-fat milk were treated by the mixed-bed column method described.

Non-fat milk of varying calcium content was tested by the milk panel by a method which measured the degree of difference between treated samples and an untreated non-fat milk. Coded controls were evaluated with the coded treated samples. For this test a 10-point scale was used in which the control was arbitrarily asigned a value of 0. A numerical value of 0.5 to 3.5 represented a slight degree of difference between treated sample and control, 3.5 to 6.5 a moderate difference and 6.5 to 10 a difference varying from large to extreme.

The degree-of-difference data for several tests compiled and averaged are shown in Table 5 and are plotted in Figure 3. Approximately 30% of the calcium of skim milk may be removed by the mixed-bed method with but a slight difference between resin-treated samples and control.

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[e] A lot of Amberlite IR-45 was found to impart a marked toluene-like odor and foreign flavor to milk treated with it. This contamination was obviated by heating the resin in a forced-draft oven at 80° C.

[f] The resins, though supplied in an active form ready for use, should be backwashed prior to use to remove any excess regenerant and to obtain resin samples of approximately uniform particle size. In backwashing the resin is placed in either a tall cylinder or an exchange column and distilled or deionized water is introduced upflow from the bottom of the column at a rate sufficient to cause approximately a 50% bed expansion and the flow is continued until the finer material has been washed up and out and the effluent water reaches a constant pH.

[g] It was found subsequent to this work that a mixture of IR-45 and IRC-50 in the ratio of 3:2 gave the least amount of change in pH of the effluent milk as compared with influent.

[h] A steel rod 60 inches in length and 3/32 inches in diameter having at one end a spiral twist 3 inches in length was used to mix the resins in the exchange column.

The principal flavor change reported for treated non-fat milk samples was increased "wateriness." Wateriness appears to be the result of a physical change in the colloid as was evidenced by a marked decrease in optical density as extent of demineralization was increased as shown in Table 6 and Figure 4. Essentially no loss in Kjeldahl nitrogen (less than 2%), a 6% loss in total solids, and a pH drop averaging 0.3 were observed with

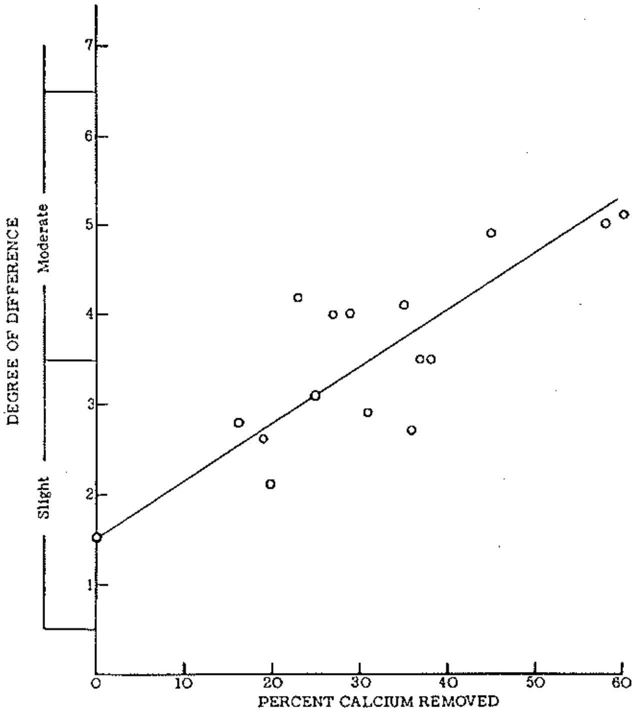

Figure 3. Degree of difference between mixed-bed demineralized non-fat milk and untreated control.

samples demineralized to the extent of 90% calcium removal.

Whole milk of varying calcium content, prepared by the mixed-bed procedure described, and coded untreated milks were tested by a 20-member milk panel using the 9-point quality rating scale previously described.

Quality ratings for several evaluations of resin-treated whole milk are shown in Table 7. Average ratings are plotted in Figure 1. Demineralization of whole milk equivalent to 50% calcium removal may be accomplished with but a slight lowering in quality rating.

Percent losses of Kjeldahl nitrogen, ash, and fat for

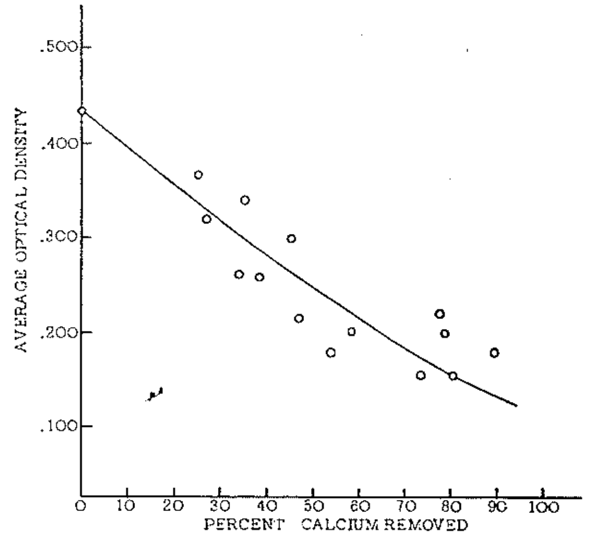

Figure 4. Optical density of 1:100 aqueous dilution of mixed-bed demineralized non-fat milk.

effluent whole milks of varying calcium content shown in Table 8 are plotted in Figure 5. It is seen that with complete decalcification approximately 80% loss of ash had occurred but only 1% of the Kjeldahl nitrogen, and 5% of the fat had been removed.

Using a mixture of IR-45 and IRC-50 in the ratio of 1:1 the pH drop in effluent milks, including those com-

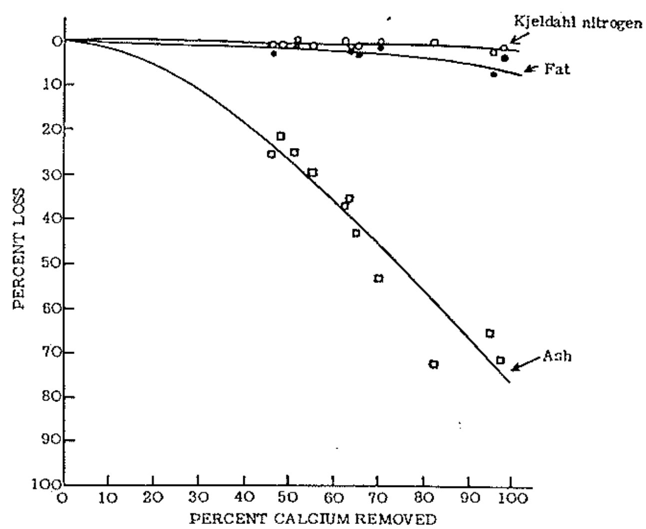

Figure 5. Percent loss of various constituents in whole milk treated by the mixed-bed procedure as a function of the percent calcium removed.

TABLE 5

Degree of difference between mixed-bed demineralized non-fat milk and untreated control using a 10-point rating scale

% Calcium removed	0	16	19	20	23	25	27	29	31	35	36	37	38	45	58	60
Mean degree of difference	1.4			2.1									3.2			5.1
	1.0		2.6									3.5			5.0	
	1.5	2.7			4.2			4.0								
	1.8					3.1				4.1				4.9		
	1.7						4.0						3.8			
	1.9	2.9							2.9		2.7					
Average mean difference	1.5	2.8	2.6	2.1	4.2	3.1	4.0	4.0	2.9	4.1	2.7	3.5	3.5	4.9	5.0	5.1

pletely decalcified, did not exceed 0.3. These resins used subsequent to this work in a ratio of 3:2 have resulted in an effluent pH lowering not exceeding 0.1 for extensively decalcified milks.

TABLE 6
Optical density of mixed-bed demineralized non-fat milk

% Calcium removed	0	25	27	34	35	38	45	47
Average optical density of 1:100 aqueous dilution	.433	.367	.319	.260	.342	.259	.301	.215
% Calcium removed	54	58	73	77	78	80	89	100
Average optical density of 1:100 aqueous dilution	.181	.201	.155	.222	.201	.155	.181	.181

TABLE 7
Quality ratings for mixed-bed demineralized whole milk and untreated control milk using a 9-point rating scale

% Calcium[1] removed	0	15	25	30	35	45	50
Quality rating	7.9	7.7	6.5		5.7		
	7.5		7.7		6.7		6.6
	7.2	7.2		7.0		5.8	
	7.5			7.0		6.6	
Average quality rating	7.5	7.5	7.1	7.0	6.2	6.2	6.6

[1] Cations other than calcium were removed; these data are in process of publication.

TABLE 8
Percent loss of various constituents in whole milk treated by the mixed-bed procedure as a function of the percent calcium removed

% Calcium removed	Nitrogen	Ash	Fat
46	1	25	3
48	1	21	1
51	0	25	1
55	1	29	1
62	0	37	0
63	1	35	2
65	1	43	3
70	0	53	1
82	0	72	0
95	2	65	7
97	1	71	3

SUMMARY

High temperature heat treatment of milk to increase its resistance to lipid oxidation is a commercial practice in the manufacture of dry whole milk and other dairy products. Denaturation of serum proteins, thought by some to be responsible for a tactual defect of reconstituted dry milk, and decreased dispersibility of casein and therefore dry milk are often undesirable resultants of this treatment. Evidence exists that partial removal of calcium from fluid milk increases protein resistance to heat induced changes.

Batch and column procedures for calcium removal employing synthetic cationic resinous exchangers singly, in series with anionic exchangers, and in intimate mixture have been described.

Sensory evaluation and pH change have been employed in comparing exchange methods. More calcium may be removed from milk with less change in sensory rating by the use of cationic and anionic resins in intimate mixture than by the use of the cationic resins either singly or in series with anionic exchangers. With but a comparatively slight change in sensory rating, approximately 10% of the calcium may be removed from whole milk using the hydrogen form of the cationic exchanger, 20% using this form in series with the sodium form, 50% using a mixture of a cationic and anionic resin and 30% from skim milk employing this mixture. Change in pH, even with extensive calcium removal, was slight when the mixed-bed procedure was employed.

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