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Reduction of Salt Content of Food Processing Liquid Waste Effluent

ENVIRONMENTAL PROTECTION AGENCY • WATER QUALITY OFFICE

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Reduction of Salt Content of Food Processing Liquid Waste Effluent

by

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for the

WATER QUALITY OFFICE

ENVIRONMENTAL PROTECTION AGENCY

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ABSTRACT

Olive brines containing 0.05 to 0.7 percent sodium chloride were passed through a mixed bed of cation and anion exchange resins. The effect of influent composition on the composition of effluent from the ion exchange unit was investigated using a range of influent pH, salt content, and C.O.D. levels. Influent pH was not a factor in the performance of the unit due to rapid pH increase from the calcium hydroxide in the resin bed. The unit was operated at sodium chloride levels of 500 to 7,000 ppm with random pH and C.O.D. levels. The highest removal of sodium chloride (94 percent) was obtained at a level of 2,700 ppm sodium chloride in the influent. With pH and C.O.D. held constant, the salt content of the influent was varied between 500 and 5,000 ppm. The effluent sodium chloride content was approximately 150 ppm at 600, 1,000 and 2,700 ppm and was 790 ppm at 6,000 ppm influent concentration.

There was evidence that the extent of sodium chloride removal was decreased as the C.O.D. of the influent increased, but this relationship was not rigorously established.

C.O.D. and B.O.D. measurements were made on influent and effluent samples, and an average B.O.D./C.O.D. ratio of 0.35 was established for olive processing water.

The resins were regenerated using a solution of calcium hydroxide. To establish the maximum salt concentration attainable in the regenerant effluent, the regenerant was repeatedly recycled through the resin bed. The sodium chloride content of recycled regenerant solutions was increased 40 percent over the influent brine level and evidence was obtained that at least a ten-fold increase was possible.

The cost of desalination of dilute food processing brines by ion exchange treatment, with calcium hydroxide as the regenerant, was estimated at $0.26 per 1,000 gallons of influent.

This report was submitted in fulfillment of Project Number 12060 DXL under the partial sponsorship of the Water Quality Office, Environmental Protection Agency.

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SECTION I

CONCLUSIONS

1. The highest percentage salt removal from olive processing waters was achieved at an influent level of approximately 2,500 ppm.

2. Repeated recycling of the regenerant resulted in increasing the salt content of the regenerant influent to a level of approximately 3,000 ppm with no indication of leveling off.

3. Pretreatment of olive processing water with activated carbon reduced deposit formation on distributors and made possible flow rates up to 10,000 gpd.

4. Pre-liming and filtration of the brine used to prepare regeneration solutions decreased regeneration cycle times to about 30 min.

5. The B.O.D./C.O.D. ratio of the product water varied with salt content and extent of pre-treatment of the influent brine; the average value of the ration was 0.35.

6. The high calcium content of the product water could be reduced by passing a gas mixture containing carbon dioxide into the raw effluent from the ion exchange unit.

SECTION II

RECOMMENDATIONS

1. The possibility of reusing the product water (with further treatments if necessary) should be tested and carefully evaluated.

2. Modifications should be made on the unit specifically to the distributors and the capacity of the desalting chamber, in order to produce 10,000 gpd of water of good quality.

3. More work should be done on brine pre-treatment (e.g., the activated carbon column) emphasizing cost factors and evaluating effect on flow-rate.

4. Results obtained on the regenerant recycling were not sufficient to establish the highest salt concentration attainable in the regenerant effluent; therefore, more work should be done on regeneration.

5. Carbonation of the final effluent should be carefully tested and evaluated as means of increasing the effluent quality and reuse potential.

SECTION III

INTRODUCTION

Many foods are prepared for consumption using sodium chloride solutions for storage, fermentation or quality grading. The liquid waste produced from such operations presents a difficult disposal problem. The discharge of the saline wastes must be done in such a way that water quality standards are maintained in the receiving waters.

The magnitude of the potential for saline pollution from food processing operations is reflected in the data presented by T. J. Powers in discussion of cucumber-pickling wastewater treatment and disposal.[1]

It has been estimated that in 1962 nine olive companies in California's Central Valley discharged about 226 million gallons of water with a level of 2,300 ppm of sodium chloride as the average concentration. A typical composite waste effluent from an olive plant had the following characteristics (all in ppm): C.O.D.= 2,400; B.O.D. = 1,250, suspended solids = 110; Chloride = 3,500. The sodium chloride discharged from food processing plants has a wide geographical base and only in specific areas is the problem acute. In those areas where low dissolved solids water is available in sufficient quantity to dilute the saline wastes to a final level of 100 - 175 ppm (chloride ion), there is little danger of violating water quality standards. However, in many areas there is insufficient fresh water available to dilute the saline waste to non-polluting levels. It is in these areas that a new technology of liquid waste handling must be demonstrated and applied.

This project presents a potentially useful technology to alleviate potential saline pollution from food processing liquid wastes. The technology is based on the removal of inorganic ions and ionizable organic compounds with a mixed bed of cation and anion exchange resins. The key feature of the technology is its use of calcium hydroxide as a regenerant for the spent resin. This technology holds promise of treating saline food processing wastes to produce a salt-free water which could be reused and a concentrated salt solution which could be returned to process after suitable treatment.

The ion exchange technology was demonstrated on olive processing water due to the critical situation in the disposal of these liquid wastes in the Madera and Tulare Counties of California. The ion exchange processing of saline wastes has the potential for extension, with little modification, to the treatment of brines from the processing of cucumbers.

New processing technology, such as in-the-jar fermentation of pickles and olives,[2,3] and salt-free storage of olives[4] may provide solutions to part of the potential saline pollution from pickle and olive production. In the case of olives, it is still necessary to use sodium hydroxide to hydrolyze bitter olive constituents, so the problem of management of large volume, low salt content, processing waters still must be solved.

Ion exchange is the most promising method currently available to treat saline wastes such as olive processing waters which contain dissolved organic compounds as well as inorganic salts. There are five ion exchange processes which have been proposed for water desalination. The characteristics of these processes are tabulated in Table 1 taken, in part, from J.I. Bregman and J.M. Shackelford, Envir. Sci. Tech. 3 (4) 336 (1969).

TABLE 1

COMPARISON OF COMPETITIVE
ION EXCHANGE PROCESSES FOR WATER DESALINATION

Name of Process	TDS in feed, ppm	Operation Scale, mgd	Cost $/1000 gallons
Sul-bi-Sul	100-1000	5	0.29
Desal	150-10,000	5-10	0.13-0.78
Sirotherm	1000	5	0.25
Asahi-Grover	1000	5	0.25-0.35
Aqua-Ion	100-10,000	0.4	0.13-0.17

It is clear from an examination of the information summarized in Table 1 that the Aqua-Ion process has a lower cost (at a much smaller scale of operation) than the other processes listed. The low cost at small scale of operation is very important because the maximum output of dilute saline waste from a single olive processing plant would probably not exceed 500,000 gpd. Figure 1 is a photograph of the pilot unit which was constructed by Aqua-Ion to treat up to 10,000 gpd of saline waste under contract to NCA in this Environmental Protection Agency supported project. Figure 2 is a schematic representation of

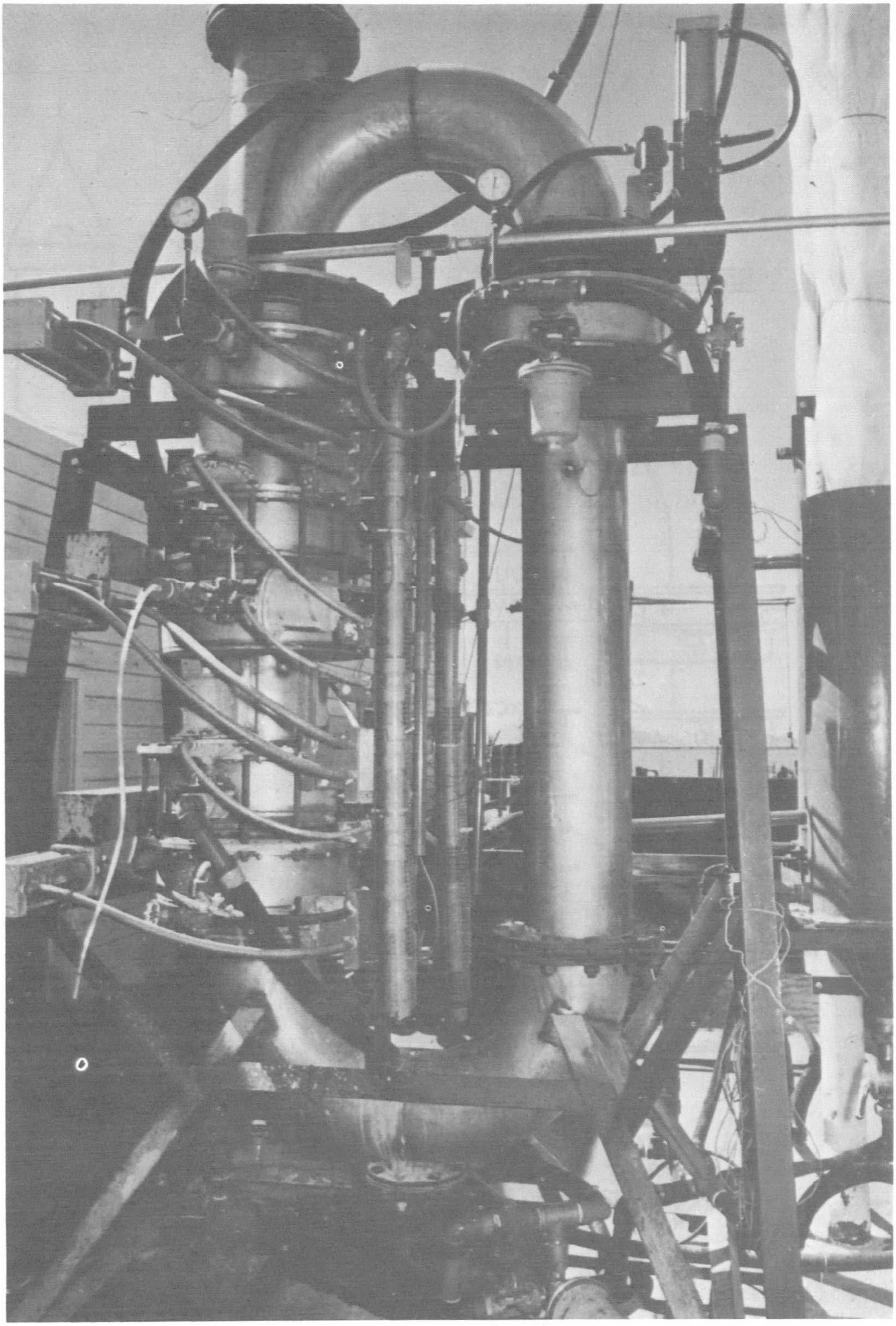

Figure 1. Photograph of the Ion-Exchange Pilot Unit

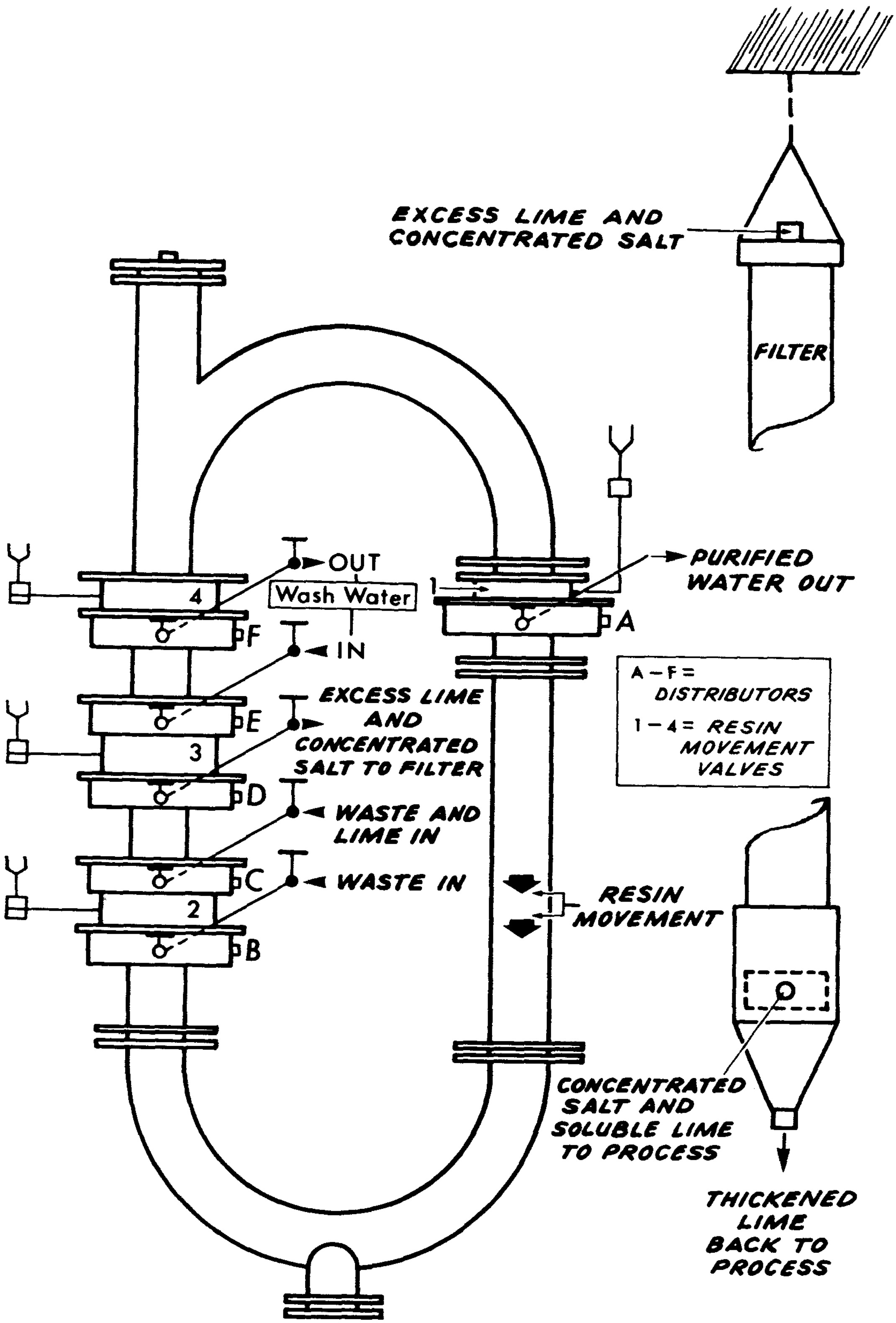

Figure 2. Schematic Representation of the Ion-Exchange Pilot Unit

TABLE 2

SPECIFICATIONS OF THE AQUA-ION ION EXCHANGE PILOT PLANT

Higgins Loop Diameter: 1 ft	
Height of Desalination Leg: 9 ft	
Resin Volume: 17.3 cu ft	
Exchanger Ratio:	65 percent cationic 35 percent anionic
Resin Movement per Cycle: 22 in.	
Uni-Flow Filters:	Primary - 20 hoses Secondary - 7 hoses
Power Rating: 7 horsepower	

the Aqua-Ion pilot unit; specifications of the unit are tabulated in Table 2. Figure 3 shows a photograph of a laboratory assembly of an ion-exchange unit.

The treatment consists of passage of waste over a mixed bed of cation and anion exchange resins. The cation exchanger was in the calcium form and was a sulfonated polystyrene resin (Duolite C-20). The anion exchanger was in the hydroxyl form and was an aminated polystyrene resin (Duolite A-102-D). The polar constituents of the waste, shown for simplicity as sodium chloride, react with the exchangers as follows:

$$\text{(cation)} \quad R_2Ca + 2\,NaCl = 2\,RNa + CaCl_2$$

$$\text{(anion)} \quad 2\,ROH + CaCl_2 = 2\,RCl + Ca(OH)_2$$

Depending on the solute concentration, the calcium hydroxide formed during the removal of sodium chloride will stay in solution or (if the

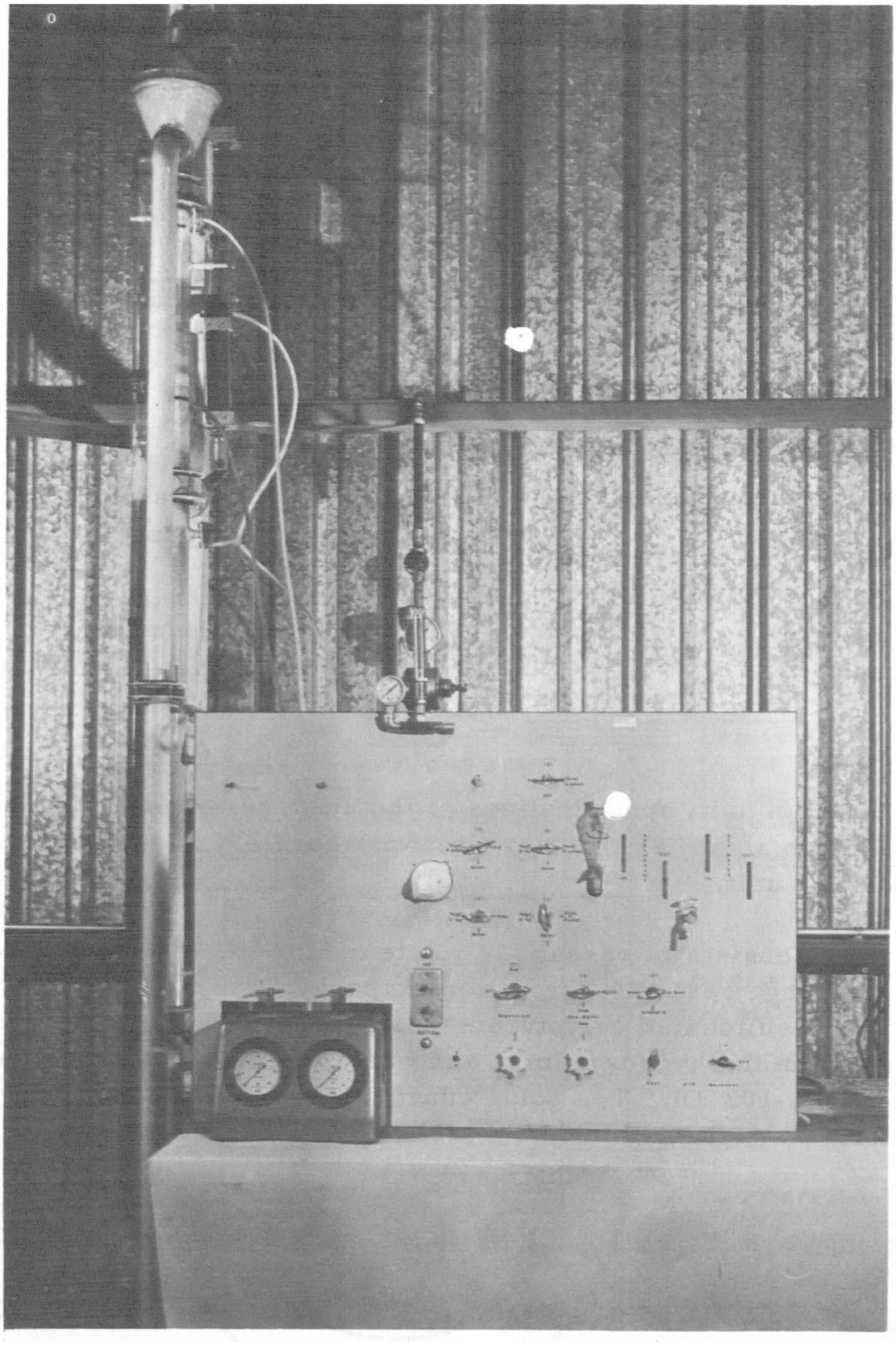

Figure 3. A Laboratory Assembly of an Ion-Exchange Unit

concentration exceeds 0.0443 N at 25°C) will precipitate. The precipitated calcium hydroxide (and other insoluble salts) can be removed using a Uni-Flow filter[5]. These filters are inexpensive and simple to use. The slurry enters the filter distributor at the top and flows down through the individual hoses. The clear liquid passes through the cloth and runs down the outside of the hose to a collection point. The sludge moves along inside the hose and is discharged periodically at the bottom (see Figures 4, 5 and 6).

The product of the ion exchange operation is a solution of calcium hydroxide and organic material. Part of the organic material originally present in the waste is converted to insoluble organo-calcium salts which can be removed by filtration. The calcium hydroxide can be removed from the ion exchange effluent by carbonation and filtration of the resulting calcium carbonate or by ion exchange of the calcium for magnesium. Formation of the insoluble magnesium hydroxide to remove calcium hydroxide is feasible in locations where either the wastewater or the water supply contains high levels of magnesium. In locations which have high bicarbonate hardness, the effluent from the ion exchange unit can be blended with hard water to produce cold lime softening as shown by the following equation:

$$Ca(OH)_2 + Ca(HCO_3)_2 = 2\ CaCO_3 + 2\ H_2O$$

The resin must be regenerated to convert it into a form usable for further sodium chloride removal. Regeneration is accomplished with a solution or suspension of calcium hydroxide in the saline wastewater. The regenerant effluent is saturated with calcium hydroxide and contains the salts and part of the organic compounds originally present in the saline wastewater. The regenerant is recycled many times in order to increase the sodium chloride concentration to a level which makes salt recovery or reuse attractive economically. The regenerated resin is rinsed with tap water to remove residual calcium hydroxide and is then ready for treatment of saline wastewater. Figure 7 shows a flow diagram of the complete ion exchange and regeneration operation.

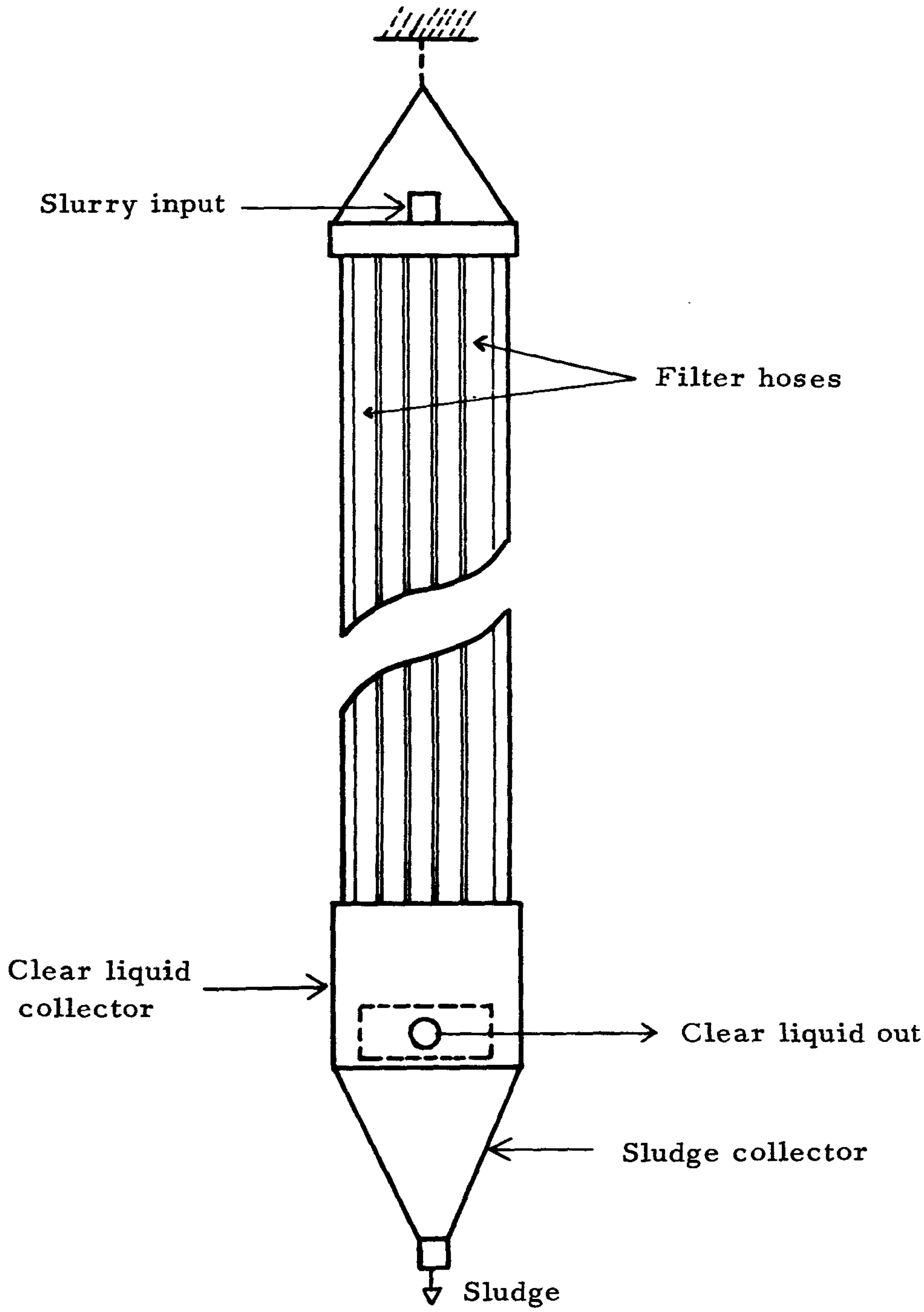

Figure 4. Schematic of a Uni-Flow Filter

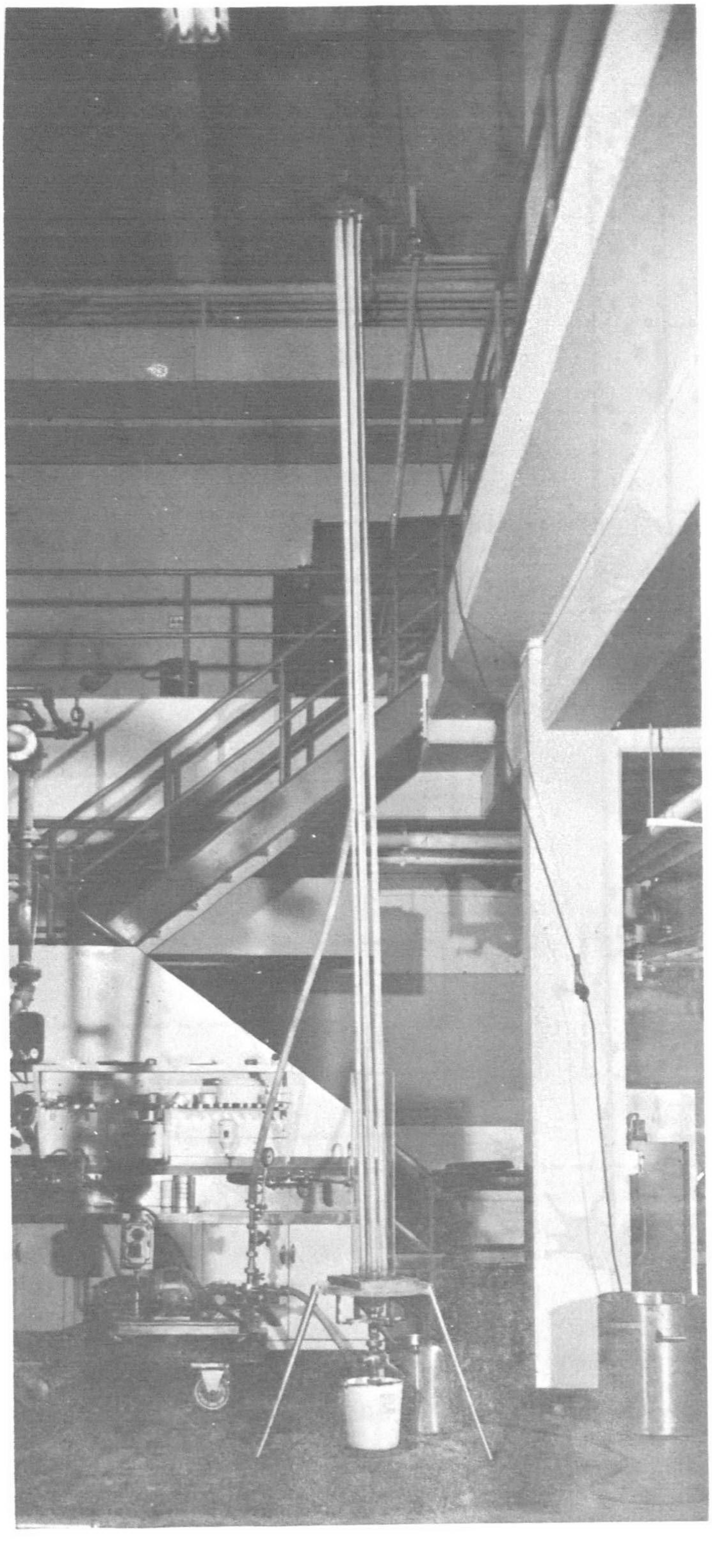

Figure 5. Photograph of a Uni-Flow Filter

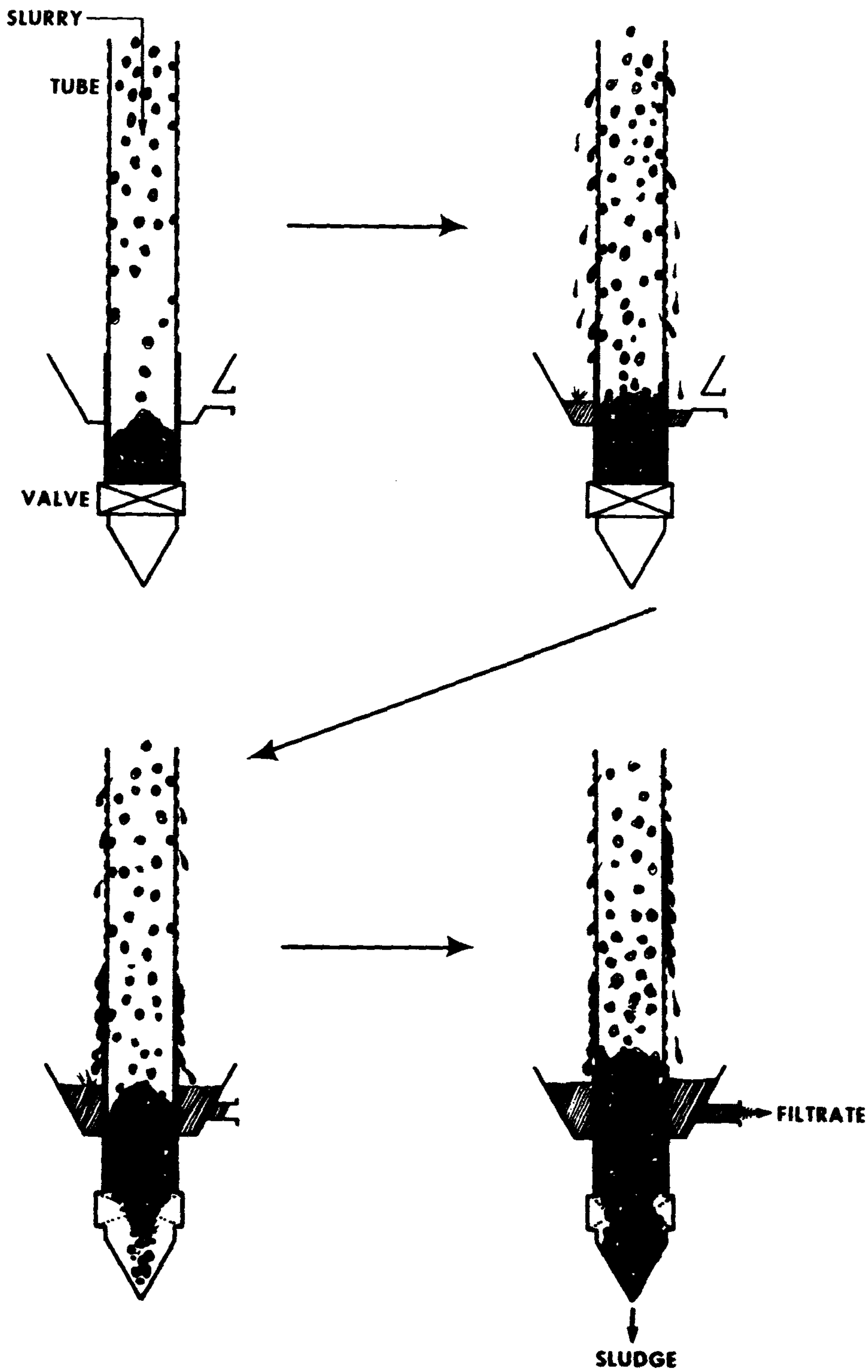

Figure 6. Schematic of Operation of a Uni-Flow Filter

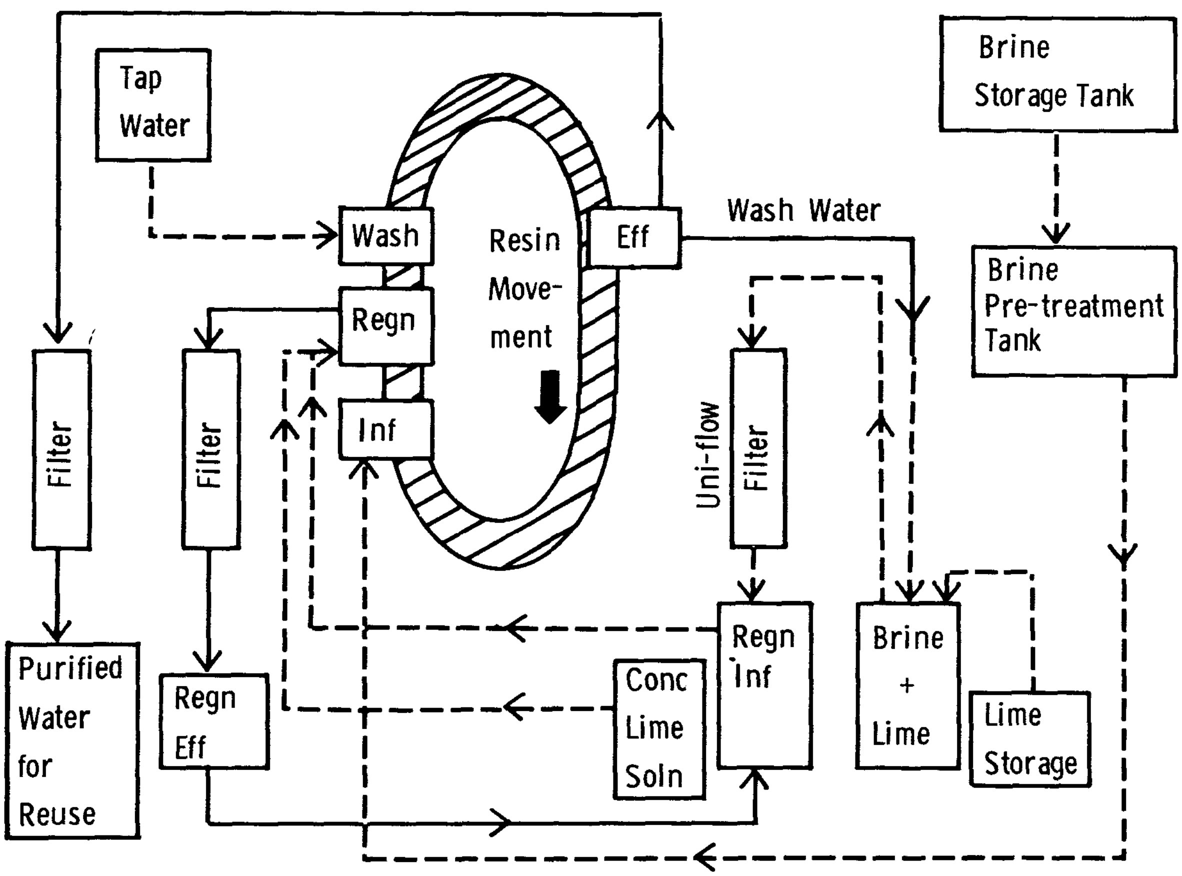

Figure 7. Flow Diagram of the Complete Ion-Exchange and Regeneration Operation

SECTION IV

OPERATION AND EVALUATION PHASE

Effect of Different Influent Salt Levels on Salt Removal

The unit was tested at different influent salt levels to determine the effect on sodium chloride removal. Runs were made with olive processing brines having sodium chloride levels of approximately 600, 1,000, 2,700 and 6,000 ppm. During these runs sodium chloride concentration was the only parameter held constant. A complete run comprises desalination, regeneration, and rinsing. Four composite samples were collected from each run and designated as: (1) influent to the unit, (2) effluent from the ion exchange unit (product), (3) regenerant influent, and (4) regenerant effluent.

The first salt level tested was approximately 600 ppm sodium chloride in the influent; this concentration was obtained by diluting olive processing water. During this series of runs the deionized effluent (product) and the regenerant influent were not filtered. Table 3 tabulates the results obtained from the analysis of composite samples collected.

These runs indicate that the sodium chloride content of olive processing water could be reduced from approximately 600 to 145 ppm. The amount of desalinated product obtained from each run was 30 to 140 gal. at a flow rate of 4 to 6 gpm. The same 150 gal. of regenerant were used for each run by recycling the effluent as influent for each successive regeneration. The color of the influent brine was light blue when the pH was relatively low and reddish-brown when the pH was high. The final effluent was usually colorless, but a few samples had a yellow color. The color of the regenerant influent and effluent was brown.

The second salt level studied was approximately 1,000 ppm as sodium chloride. Filtration was used to remove the insoluble organo-calcium compounds from the regenerant suspension and the solids from the product. The usual four samples were collected from the last run on each day of sampling by NCA personnel. Table 4 tabulates the results obtained by analysis of these samples. The salt content was reduced to a level of 168 ppm on the average in this series of runs. In runs B, C, D and E, hydrochloric acid was added to the olive

TABLE 3

ANALYSIS OF COMPOSITE SAMPLES COLLECTED
DURING THE 600 PPM SALT LEVEL PERIOD

Run No.	Sample Number	pH	NaCl, ppm	SS, ppm	C.O.D., ppm
600-A*	1	7.4	610	9	154
	2	10.9	60	128	2
	3	11.6	610	29	85
	4	11.6	605	47	104
600-B	1	9.5	590	7	183
	2	11.4	113	113	101
	3	12.0	6370**	4244***	141
	4	12.1	6960**	5868***	134
600-C	1	11.0	600	14	158
	2	12.1	330	225	150
	3	11.8	630	852	161
	4	12.1	590	5956***	173

* A, B, and C are three different sets of samples collected on three different days. Samples represent the last run on each of these days.

** These unusually high values were due to residues of hydrochloric acid used to clean distributors.

*** These high values were due to suspended excess calcium hydroxide.

processing water to adjust the pH to about 7. The volume of desalinated product from an individual run was 45 to 60 gal. at a flow rate of 3 to 4.5 gpm. Regeneration was accomplished using recycling of the 150 gal. used for the run 1000-A.

Several runs were completed with a salt level of approximately 2,700 ppm sodium chloride in the influent. The desalinated product averaged 155 ppm sodium chloride content as shown in Table 5. The color of the influent brine was reddish-brown and the desalinated product was yellow. The regenerant influent and effluent were both yellow. The volume of product was 20 to 50 gal. at a flow rate of 3 to 4.5 gpm. Regeneration was accomplished by recycling 150 gal. of regenerant four times.

TABLE 4

ANALYSIS OF COMPOSITE SAMPLES COLLECTED DURING THE 1000 PPM SALT LEVEL PERIOD

Run No.	Sample Number	pH	NaCl, ppm	SS, ppm	C.O.D., ppm
1000-A	1	10.6	1195	60	333
	2	11.5	190	3	115
	3	12.0	1180	30	340
	4	12.0	1117	150	290
1000-B	1	6.9	1190	2	356
	2	11.0	50	10	131
	3	12.0	1150	20	370
	4	12.0	1165	200	350
1000-C	1	6.8	1305	2	265
	2	12.0	90	0	86
	3	12.1	1340	0	214
	4	12.1	1320	10	187
1000-D	1	7.2	1195	16	N.R.*
	2	12.4	305	0	N.R.
	3	12.4	985	6	N.R.
	4	12.5	1095	9	N.R.
1000-E	1	7.4	1170	19	N.R.
	2	12.5	205	4	N.R.
	3	12.5	995	17	N.R.
	4	12.6	1070	11	N.R.

* N.R. - Not recorded.

An influent brine of approximately 6,000 ppm sodium chloride content was passed through the ion exchange unit as the fourth salt level to be tested. The results from analysis of eight groups of samples collected during this part of the project are tabulated in Table 6. The desalinated product had an average salinity of 790 ppm as sodium

TABLE 5

ANALYSIS OF COMPOSITE SAMPLES COLLECTED
DURING THE 2700 PPM SALT LEVEL PERIOD

Run No.	Sample Number	pH	NaCl, ppm	C.O.D., ppm	Ca, ppm	$CaCO_3$, ppm
2700-A	1	8.1	2500	1236	35	88
	2	12.4	295	735	766	1910
	3	12.4	1775	1093	470	1180
	4	12.4	1975	968	920	2290
2700-B	1	7.8	2750	359	24	59
	2	12.0	86	210	210	520
	3	12.3	2290	1258	660	1646
	4	12.4	2500	1176	870	2170
2700-C	1	7.6	2725	1367	24	59
	2	11.8	125	512	106	265
	3	12.3	2450	1367	412	1029
	4	12.4	2605	1179	884	2205
2700-D	1	8.2	2795	1333	12	29
	2	11.7	160	453	47	118
	3	12.5	2290	1201	590	1470
	4	12.5	2300	1101	719	1793
2700-E	1	8.0	2750	562	12	30
	2	11.8	130	320	51	130
	3	12.2	2390	485	283	706
	4	12.5	2400	440	1184	2950

chloride. The volume of regenerant used for this series of runs was reduced to about 100 gal. per run and was recycled in sets of 3 or 4 runs.

To follow changes in the extent of salt removal which occur during the duration of individual runs, grab samples were collected for each 10 gal. of effluent up to 50 gal. In addition, the usual 50 gal. composite sample was obtained. These samples were analyzed for chloride ion; the results are tabulated in Table 7. Figures 8, 9 and 10 illustrate the results graphically.

TABLE 6

ANALYSIS OF COMPOSITE SAMPLES COLLECTED DURING THE 6000 PPM SALT LEVEL PERIOD

Run No.	Sample Number	pH	NaCl, ppm	C.O.D., ppm	Ca, ppm	$CaCO_3$, ppm
6000-A	1	7.0	6810	1489	12	29
	2	11.9	490	234	318	794
	3	12.0	5700	1251	704	1705
	4	12.1	4650	1003	1072	2675
6000-B	1	7.3	6710	1510	12	29
	2	12.3	750	602	365	911
	3	12.4	5610	1219	754	1882
	4	12.5	5610	1111	1084	2705
6000-C	1	7.0	7050	1436	12	29
	2	11.9	850	266	236	590
	3	12.1	5720	1231	625	1560
	4	12.1	5250	1029	1108	2764
6000-D	1	7.1	5890	1143	18	44
	2	12.0	840	474	212	529
	3	12.2	5790	1209	660	1646
	4	12.2	5820	1067	2286	5703
6000-E	1	7.7	4950	1238	22	54
	2	11.2	1150	797	184	460
	3	11.7	2590	178	921	2299
	4	11.8	3010	257	1333	3327
6000-F	1	7.4	5590	1163	12	29
	2	11.7	490	176	212	529
	3	11.8	5420	1069	707	1764
	4	11.8	5310	930	1108	2764
6000-G	1	6.7	5290	969	12	29
	2	11.7	890	367	282	705
	3	11.7	5650	1014	695	1734
	4	11.8	4690	731	1120	2793
6000-H	1	6.9	5250	929	12	29
	2	11.9	840	346	212	529
	3	11.9	5720	927	577	1441
	4	12.0	3990	546	1025	2558

TABLE 7

REDUCTION IN SALT CONTENT DURING AN INDIVIDUAL RUN

Batch A				Batch B				Batch C			
	Inf	Eff			Inf	Eff			Inf	Eff	
Run No.	Cl, ppm	gal.	Cl, ppm	Run No.	Cl, ppm	gal.	Cl, ppm	Run No.	Cl, ppm	gal.	Cl, ppm
1	1132	10	300	1	1240	10	284	1	1017	10	331
		20	288			20	248			20	281
		30	240			30	221			30	255
		40	215			40	209			40	231
		50	203			50	209			50	221
		comp.	248			comp.	237			comp.	265
2	1132	10	306	2	1240	10	335	2	1450	10	297
		20	304			20	301			20	296
		30	289			30	259			30	273
		40	259			40	237			40	248
		50	236			50	221			50	245
		comp.	280			comp.	272			comp.	266
3	1132	10	284	3	1240	10	396	3	1450	10	278
		20	274			20	389			20	273
		30	243			30	363			30	238
		40	223			40	313			40	205
		50	203			50	246			50	185
		comp.	252			comp.	348			comp.	239

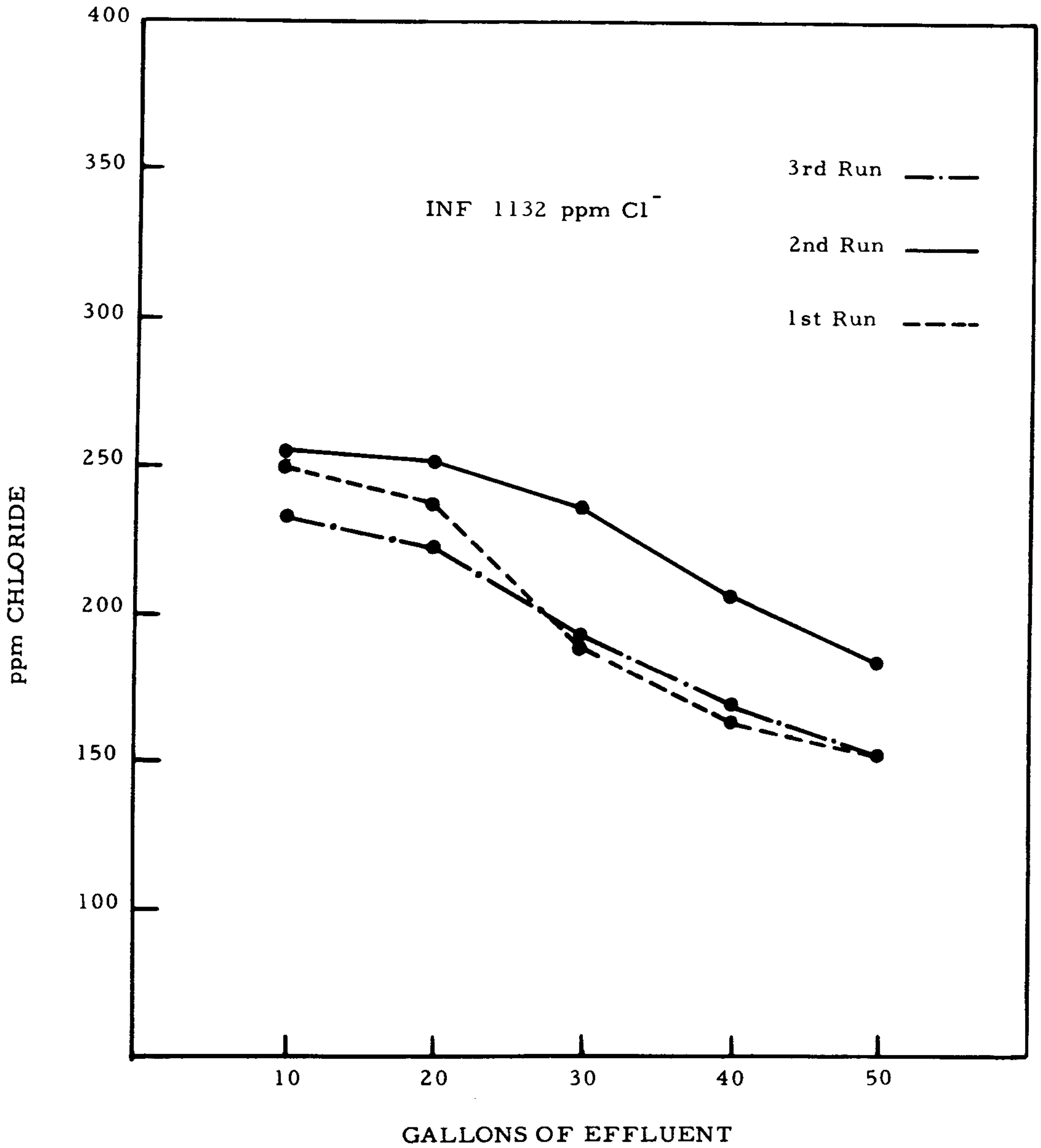

Figure 8 The Gradual Salt Reduction During An Individual Run

Batch A

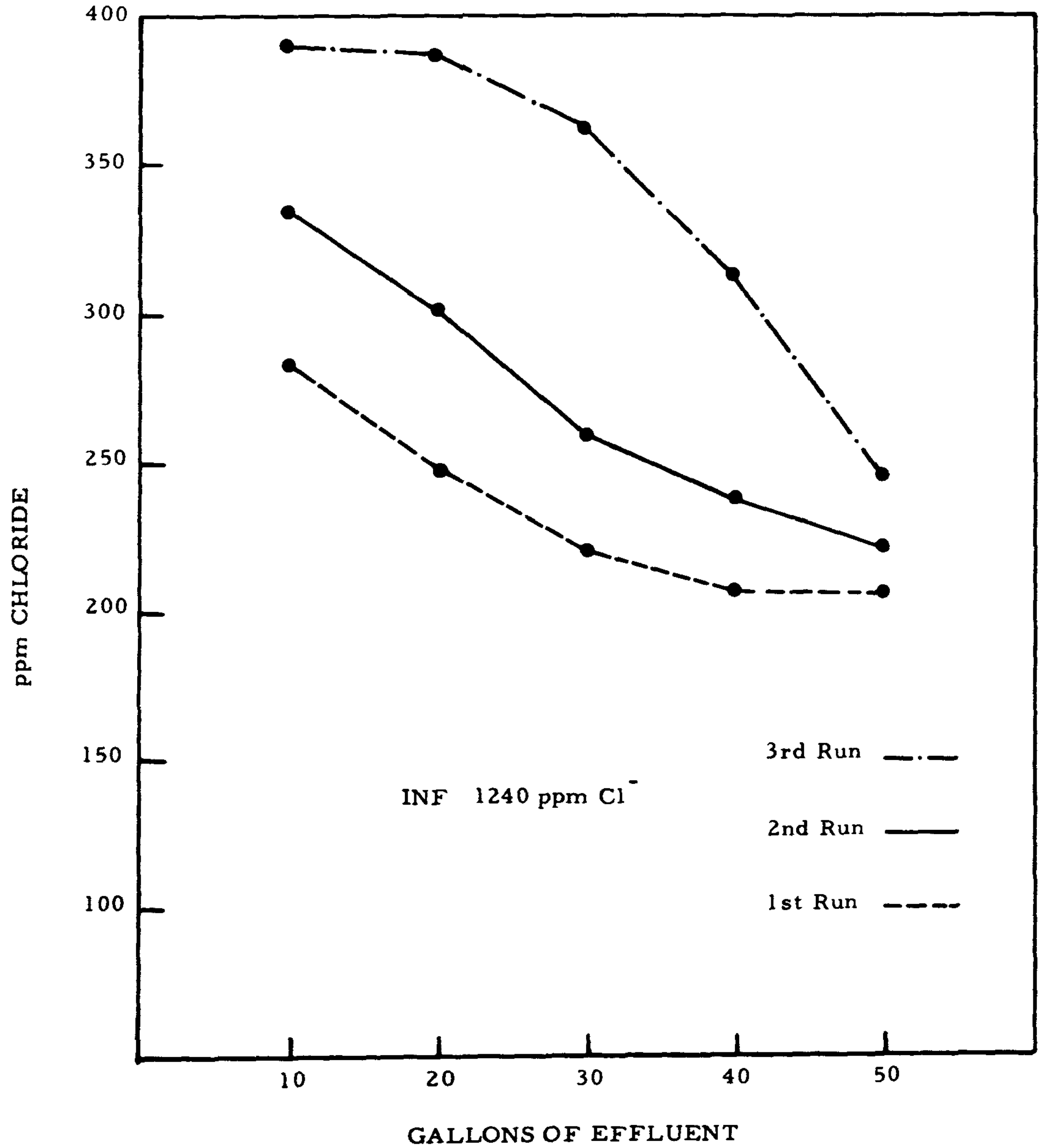

Figure 9 The Gradual Salt Reduction During An Individual Run

Batch B

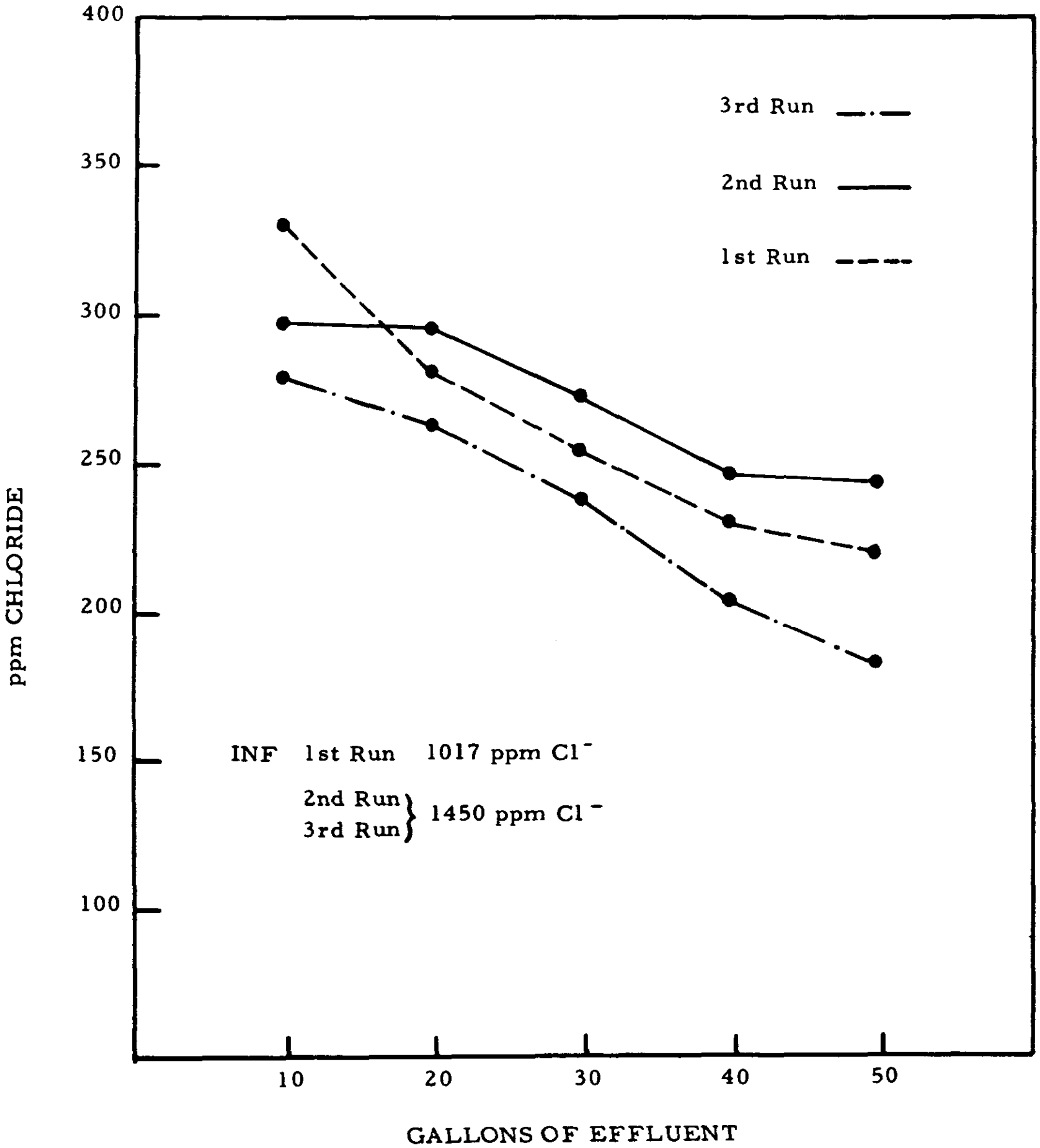

Figure 10 The Gradual Salt Reduction During An Individual Run

Batch C

Effect of pH on Sodium Chloride Removal

Under the experimental conditions used in this project, pH was found to have no significant influence on salt removal. This observation can be explained by the fact that the resin was in the calcium or hydroxyl form or, at times, in a carbonate form. When the influent olive processing water contacted the resin, the pH was increased to the alkaline side of 7 regardless of the influent pH level. Differences in performance due to pH changes would be expected if the resin bed had been fully converted to the sodium and chloride forms; no such condition was observed during the project.

Effect of Chemical Oxygen Demand Level on Salt Removal

No effect on salt removal would be expected from traces of non-polar organic compounds present in the influent brine. If neutral organic compounds were present in the influent in large amounts, they could coat the resin and decrease the salt removal efficiency. A more severe problem would exist if the organic compounds in the influent were polar in nature, since they would compete for active sites on the resin with sodium and chloride ions. This competition would reduce the desalting efficiency of the resin bed. Neither extreme of these two situations was experienced in this project since the C.O.D. content of the influent did not exceed 1,600 ppm. There was evidence that the salt removal was decreased as the C.O.D. of the influent increased, but this relationship was not rigorously established.

A B.O.D./C.O.D. ratio was calculated for olive processing wastewater having sodium chloride levels of 2,500 and 5,000 ppm. A similar ratio was established for the desalinated product water obtained from the ion exchange treatment of these brines. The data collected for the calculation of the ratios is tabulated in Table 8. The ratio varied with the salt content and the extent of treatment of the brine samples. The average value of the B.O.D./C.O.D. ratio was 0.35.

Effect of Ion Exchange Treatment of Olive Processing Waters on C.O.D. Level in Desalinated Product

The ion exchange treatment of olive processing water was expected to remove ionized and ionizable organic compounds. The detailed

TABLE 8

B.O.D.$_5$:C.O.D. RATIO
FOR OLIVE PROCESSING WASTEWATERS

Wastewater				Desalinated Product		
NaCl, ppm	C.O.D., ppm	B.O.D., ppm	B.O.D., / C.O.D.,	C.O.D., ppm	B.O.D., ppm	B.O.D., / C.O.D.,
2500	560	200	0.36	290	130	0.45
2500	760	320	0.42	340	120	0.35
2500	700	290	0.41	330	110	0.33
2500	660	260	0.39	320	120	0.37
2500	630	230	0.37	370	130	0.35
2500	610	270	0.44	310	150	0.48
	Average Value		0.40			0.39
5000	1490	470	0.32	230	70	0.30
5000	1510	470	0.31	600	170	0.28
5000	1440	360	0.25	270	70	0.26
5000	1140	310	0.27	470	140	0.30
5000	830	340	0.41	430	110	0.26
5000	1160	480	0.41	180	70	0.39
5000	970	230	0.24	370	100	0.27
5000	930	260	0.28	350	90	0.26
	Average Value		0.31			0.29

composition of olive processing water is not known, but such compounds as acetic acid, lactic acid, citric acid, saccharic acids, and hydrolyzed pectins are probably present. The Aqua-Ion technology would remove these compounds either by binding on the resin (to be released later during regeneration) or by formation of insoluble calcium salts (removed by filtration). Examination of the data tabulated in Tables 3 through 6 indicates that substantial quantities of organic materials in the olive processing waters are removed during the ion exchange treatment. In some cases, as much as 85 percent of the initial C.O.D. material was removed by treatment and filtration. The effect of residual C.O.D. materials in the desalinated product water on the reuse potential is of importance, but was not evaluated in this project.

Effect of Different Salt Levels in Influent Brines on the Salt Removal at Constant C.O.D. and pH

Olive processing brines having an initial sodium chloride content of approximately 600, 1,000, 2,400 and 5,500 ppm were passed through the ion exchange unit. Suspended solids were eliminated from consideration as a variable in this part of the study, since the influent brine was filtered through a Uni-Flow filter before entering the ion exchange unit. Therefore, C.O.D. and influent pH were the only compositional factors which were adjusted to relatively constant values. The adjustment of the C.O.D. content was made by the addition of lactic acid to the olive brine until a value of about 800 ppm was reached. The pH was adjusted at about 7.5 by the addition of strong sodium hydroxide solution. One set of samples was collected and analyzed for each of the four salt levels; the results are tabulated in Table 9. The effluent was approximately the same until the salt level in the influent exceeded 2,400 ppm.

TABLE 9

ANALYSIS OF COMPOSITE SAMPLES OF FOUR DIFFERENT SALT LEVELS WITH C.O.D. AND pH HELD CONSTANT

Sample Number	NaCl, ppm	C.O.D., ppm	pH	Ca, ppm	$CaCO_3$, ppm
1	590	805	7.4	22	54
2	190	217	10.6	44	108
3	490	29	11.9	1323	3300
4	1100	191	11.6	542	1352
1	1070	958	7.5	22	54
2	250	151	10.8	33	81
3	1150	45	11.6	444	1109
4	1350	146	11.8	737	1839
1	2380	797	7.3	22	[illegible]
2	210	465	10.7	44	[illegible]
3	2410	91	11.7	2483	6194
4	2450	137	11.6	750	1785
1	5510	830	6.9	12	29
2	1150	426	12.3	636	1587
3	5150	1029	12.2	730	1823
4	4650	816	12.3	2510	6262

Establishment of the Maximum Sodium Chloride Concentration Attainable in the Regenerant Effluent

The maximum sodium chloride concentration possible in the regeneration effluent is of considerable economic importance in evaluating the overall usefulness of ion exchange treatment of food processing brines. Ideally, both the product water and the concentrated regenerant solution could be recycled in selected stages of the food processing operation. If both of these objectives cannot be accomplished, concentrating the salt present in the treated processing water in a small volume would make further management less costly. To establish the maximum sodium chloride concentration attainable in the regenerant effluent, the liquid from each of a large number of resin regeneration runs was recycled after each individual run. To determine the increase in salt concentration in the regenerant effluent, a composite sample was taken from each effluent and the sodium chloride content was determined. The results of this investigation are tabulated in Table 10. The average increase in salt content in the regenerant effluent was approximately 40 percent (difference between original influent and last effluent of a recycle series), depending on the salt level and the flow rate.

It was found that the salt increase in the regenerant suspension occurs at a slow rate. There was not sufficient operating experience with any single influent brine composition to determine the maximum salt concentration attainable in the regenerant. A test was run using a concentration of approximately 20,000 ppm sodium chloride made by adding solid salt to an olive processing water. The use of this solution in regeneration gave an average increase in sodium chloride in the regenerant effluent of 595 ppm. This result indicated that it was possible to have substantial salt increases in the regenerant effluent even at salt levels of approximately 2 percent.

Effect of Cycle Time on Regeneration

The work on regeneration was continued using different cycle times. Table 11 tabulates the sodium chloride content of regenerant effluent and influent at various cycle times. The influent sodium chloride concentration was 1,900 to 3,500 ppm in these runs and the flow rate was 4.5 gpm. The regenerant effluent was recycled. The cycle time was calculated by dividing the gal. of influent used in a run by the flow

TABLE 10

INCREASE IN THE SODIUM CHLORIDE CONTENT OF REGENERANT EFFLUENT AS A RESULT OF REGENERANT RECYCLING

Run No.	Flow Rate, gpm	NaCl, ppm Inf	NaCl, ppm Eff	Run No.	Flow Rate gpm	NaCl, ppm Inf	NaCl, ppm Eff
1 A	2	2070	2180	1 R	6	1790	1856
2 A		2300	2360	2 R		1860	2086
3 A		2480	2720	3 R		1879	2106
1 B	2	2410	2820	4 R		1948	2131
				5 R		1983	2135
1 C	2	2590	2910	1 T		2390	2516
2 C		2600	2750	2 T		2322	2434
3 C		2660	2930	3 T		2416	2486
1 D	2	2540	2770	4 T		2468	2490
2 D		2630	2890	1 U		2521	2633
3 D		2670	3040	2 U		2516	2785
4 D		2710	3190	3 U		2580	2668
1 E	2	2760	3030	4 U		2565	2673
2 E		2790	3140				
3 E		2860	3090	1 S	7	2012	2173
1 F	2	2940	3310	2 S		2011	2112
2 F		2910	3370	3 S		2200	2280
1 G	2	2920	3220	4 S		2190	2311
2 G		2970	3220				
1 H	2	3030	3110	1 O	8	1229	1280
2 H		2970	2990	2 O		1132	1252
				3 O		1188	1451
1 I	2	3000	3070	4 O		1429	1633
2 I		3050	3220				
1 J	2	3070	3730	1 Q	9	2416	2808
				2 Q		2562	2890
1 L	3	924	2451*	3 Q		2896	2907
2 L		895	708	4 Q		2750	2867
3 L		866	942				
1 M	3	820	1106	1 K	3	20,534**	20,622
2 M		1024	1103	2 K		20,885	21,762
				3 K		20,124	20,943

* High value due to cleaning of distributors with HCl.

** Salt content of the influent increased by adding NaCl.

rate of 4.5 gpm. The maximum sodium chloride content increase was obtained with a cycle time of 30 min. The difference between the 10 and 20 min cycle times was not significant.

TABLE 11

SODIUM CHLORIDE CONTENT OF THE REGENERANT INFLUENT AND EFFLUENT AT VARIOUS CYCLE TIMES

Cycle Time, min	NaCl, ppm		Cycle Time, min	NaCl, ppm	
	Inf	Eff		Inf	Eff
10	1983	2135	40	2738	2849
	2318	2363		2738	2884
	2306	2451		2750	2890
				2770	2972
20	2516	2785		2785	2925
	2580	2668		2785	2984
	2565	2673		2790	2890
				2799	3177
30	2321	2790		2808	2907
	2594	2878		2828	2880
	2615	2837		2843	3024
	2650	2790		2858	3010
	2714	2937		3001	3060
	2732	2948		3352	3732
	2998	3179		3472	3674
	3033	3136			
	3117	3146			

Continuous Operation to Develop Treatment Cost Figures

In this phase of the study the time between the various unit operations, e.g., desalination, regeneration and rinsing, was kept to a minimum. Only 20 to 30 sec were required to pulse the resin between the runs. The only significant interruption was the time needed for fresh brine make-up.

In preparation for continuous operation, the regeneration chamber was washed with a solution of hydrochloric acid to remove the organo-calcium compounds which had precipitated on the plastic beads holding the resin above the distributor screen. This treatment resulted in regenerant flow rates as high as 10 gpm. However, after a short time the flow rate decreased due to plugging of the distributors by calcium carbonate and organo-calcium compounds. The sodium chloride content of the influent brine during this continuous operational period was 1,000 to 1,900 ppm and the flow rate was varied from 3.0 to 7.5 gpm. Table 12 tabulates the reduction in sodium chloride content of the influent brine as the unit was operated continuously at different flow rates.

TABLE 12

REDUCTION IN SALT CONTENT OF INFLUENT BRINE OBTAINED DURING THE CONTINUOUS OPERATION OF THE UNIT AT DIFFERENT FLOW RATES

Run No.	Flow Rate, gpm	Inf NaCl, ppm	Eff Vol, gal.	NaCl, ppm	Run No.	Flow Rate, gpm	Inf NaCl, ppm	Eff Vol, gal.	NaCl, ppm
CA- 1	4.5	1761	50	642	CE-1	5.0	1526	30	652
2	4.5		50	900	2	5.0		30	623
3	4.0		30	784	3	5.0		30	578
4	4.5		30	670	CF-1	5.0	1508	30	720
5	3.5		30	690	2	5.0		30	641
CB-1	4.5	1854	30	543	3	5.0		30	610
2	4.0		30	525					
3	4.0		35	562	CG-1	7.5	1740	30	1211
4	3.5		30	573	2	7.0		30	1030
CC-1	4.5	1878	30	465	3	7.5		35	860
2	4.0		30	453	CH-1	7.0	1740	30	525
3	4.0		30	470	2	7.0		30	544
4	3.5		30	452	3	7.0		30	550
CD-1	3.5	1053	30	294	CI- 1	7.5	1547	30	1508
2	4.0		30	274	2	7.0		30	1110
3	4.0		30	273	3	7.0		30	878

Hardness in Product Water from Ion Exchange Treated Brines

The use of calcium hydroxide as a regenerant in the Aqua-Ion technology causes this material to appear in the desalination product and results in a hard water of limited reuse potential without additional treatment.

TABLE 13

CALCIUM ION CONCENTRATION AND HARDNESS OF THE INFLUENT AND EFFLUENT OF BOTH THE DESALINATION AND REGENERATION PROCESSES

Run Number	Sample Number*	Ca, ppm	Hardness as $CaCO_3$, ppm
H-A	1	33	83
	2	835	2083
	3	713	1778
	4	1091	2722
H-B	1	22	56
	2	668	1667
	3	701	1750
	4	935	2334
H-C	1	47	120
	2	800	2000
	3	870	1940
	4	990	2470

* Samples are the same as those in previous tables.

Calcium ion concentration was determined on a large number of the usual set of four samples collected from individual runs under a wide range of conditions. Table 13 tabulates the calcium ion concentration and hardness as calcium carbonate for typical samples.

Extension of Ion Exchange Treatment to Brine from Other Commodities

The use of ion exchange treatment of dilute brines has promise for reducing the saline pollution potential of liquid wastes from preservation of cabbage, cherries and pickles. New information was obtained during this project on the composition of brines used to store cherries and cucumbers. The final products of these storage systems were Maraschino cherries and dill pickles. Arrangements to obtain brine

TABLE 14

ANALYTICAL VALUES FOR BRINES
USED IN MARASCHINO CHERRY AND
DILL PICKLE PRODUCTION

Product	pH	NaCl, ppm	SS,* ppm	C.O.D.,* mg/liter	B.O.D.,* mg/liter	Hardness Ca, ppm	CaCO$_3$, ppm
Cherry	6.6	95	20	590	330	82	205
Cucumber	3.6	39,900	95	3,936	2,480	589	1,470

* Determined by FWPCA Official Interior Methods for Chemical Analysis of Waters, September, 1968

from storage of cabbage for sauerkraut were terminated when it was learned that all of the brine is used as the liquid portion of the canned sauerkraut or as canned sauerkraut juice. The results of analysis of cherry and cucumber brines are tabulated in Table 14.

SECTION V

DISCUSSION

Salt Removal

In general, the salt removal obtained was satisfactory. The results demonstrated that desired product quality can be obtained at varying levels of polar solute concentration when C. O. D. and pH are relatively constant. At 5,000 ppm sodium chloride concentration, the salt content of the product was higher than the target value of 175 ppm. The influent salt level was not believed to be the cause of the higher level of sodium chloride in the product water. Rather, the observed result could be attributed to intermixing which took place through the resin bed and caused displacement of the salt front. The intermixing problem was encountered during several periods of operation of the ion exchange unit. Near the end of the project a technique was found to minimize intermixing in the resin bed. On completion of a regeneration cycle, valve No. 3 and an additional outlet valve (just prior to valve No. 2 on Figure 2) were opened. Compressed air was used to push out the regenerant effluent and the water filling the wash chamber. In this way, the contact between the regenerant and the final product at the top of the Higgins Loop was avoided. The quality of the final product was improved substantially when this procedure was applied. The salt content was reduced from 1,500 ppm in the influent to a range of 130 to 270 ppm in the desalination product. The unit was operated at 4 gpm during this use of the revised procedure. It was unfortunate that more time was not available to study all the variables examined and reported above which were obtained under less than optimal operating conditions.

Conventional Regeneration

Slaked lime ($Ca(OH)_2$) performed successfully in regenerating spent resin used to desalinate the olive processing brines. The recycling of the regenerant effluent increased the sodium chloride content of the regenerant. The long term trend of sodium chloride increase was apparent from examination of data in Table 10, although the difference in salt content in any pair of adjacent runs did not appear to be significant (for example, Run No. 1C and Run No. 3C). This was due to the diluting effect of the wash water filling the void space of the resin.

The void space can represent as much as 40 percent of the total volume of the resin.

At high flow rates, when distributors tend to plug up, washing with acid solution was required to open up the flow channels. The residues of hydrochloric acid solution resulted in sudden increases in the chloride ion readings for some effluent samples. The pre-liming and filtration of the regenerant influent resulted in shorter regeneration times and longer operational periods with fewer acid washings being required.

Within the time limit assigned to any given phase of the project, the average increase in the sodium chloride concentration of the regenerant solution was approximately 40 percent. There was no indication of a leveling off of the rate of sodium chloride increase in the regenerant effluent with increasing number of cycles.

The best regeneration cycle time was found to be 30 min.

Carbonate Regeneration

One of the reasons that higher than expected sodium chloride levels were observed in certain runs was because the resin was in a calcium carbonate form rather than a calcium hydroxide form.

The equations for the reactions involved in carbonate regeneration are the following:

(Cation) $R_2Ca + 2\ NaCl = 2\ RNa + CaCl_2$

(Anion) $R_2CO_3 + CaCl_2 = 2\ RCl + CaCO_3$

When the resin was partially or completely in the calcium carbonate form, the salt removal was about 50 percent of that found for resin in the calcium hydroxide form. The relatively low calcium content of the desalinated product effluent shown in Table 15 was the result of removing most of the calcium as calcium carbonate. The sludge formed from the filtration of the desalinated product water was found to contain substantial amounts of calcium carbonate.

TABLE 15

EFFECT OF THE CARBONATE REGENERATION ON THE CALCIUM CONTENT OF THE PRODUCT WATER

Run	Inf*			Eff*		
No.	NaCl	Ca	$CaCO_3$	NaCl	Ca	$CaCO_3$
CO3 A	1590	43	108	690	54	135
CO3 B	2850	12	29	1190	71	176
CO3 C	2950	12	29	1290	47	118
CO3 D	1050	24	59	430	6	15
CO3 E	1150	24	59	570	12	29
CO3 F	1980	35	88	590	47	118
CO3 G	1650	33	81	590	43	108

* All results are in ppm.

The introduction of carbon dioxide into the ion exchange system is the reason for the appearance of carbonate regeneration. The carbon dioxide could have been introduced at the following points.

A. In the compressed air used to move the resin. If this were the source, it could be corrected by passing the air through an alkaline solution before compression.

B. In the lime used for the preparation of the regenerant influent. Samples of lime were found to contain large quantities of calcium carbonate. This could be corrected by storing the lime in tightly closed containers.

C. In gas transfer through the cloth of uncovered filter hoses. The plastic wrapping of the filter hose was occasionally torn by strong winds; a combination of low temperatures and rain wetting the hoses could promote the uptake of atmospheric carbon dioxide.

The problem of carbonate regeneration could be eliminated by operating the unit at slower rates or by employing a larger desalination leg. The second change would be the most economical way to correct for the possibility of carbonate regeneration in a scaled-up production unit.

The filtration of the regenerant and the desalinated product was not possible in a few runs due to the oxidative degradation of the cotton filter hoses. The perforation of the Uni-Flow filters on these occasions was the reason for the high suspended solids content of some samples and for the very high values for calcium and suspended solids in certain of the regenerant suspensions. The perforation of filter hoses can be forestalled by good maintenance; hoses should be replaced when they show signs of deterioration.

The desired quality of the desalination product was obtained under most operating conditions. Under certain conditions, the sodium chloride content would be considered high. However, in some areas of California the total dissolved solids content of municipal water supply range from 410 to 1,243 ppm.[6]

The desalinated product is a hard water and its calcium content should be reduced in order to increase reuse options.

The sodium chloride content of recycled regenerant solutions was increased 40 percent over the influent brine level and evidence was obtained that a ten-fold increase was possible. Stated in another way, the sodium chloride present in the original olive processing water was potentially concentrated in one-tenth of the original volume. At the same time, a volume of desalinated water equal to the volume of the treated olive processing brine was produced for possible reuse.

Examination of the data summarized in Table 14 indicates that the use of ion exchange treatment of cherry processing brine would have little utility. The very low sodium chloride level and moderately high calcium level would not be changed significantly by the Aqua-Ion process. The Aqua-Ion technology appears to be highly promising in the treatment of liquid wastes from pickle production. The high values for NaCl, B.O.D., and hardness, along with low SS and pH, suggest that pickle processing water could be treated effectively for recycle with no concern from high calcium levels in the product water. The regenerant brine has good promise of use in storage systems for freshly harvested cucumbers.

The cost of desalting 1,000 gallons of olive processing water was estimated at 26 cents (Table 16). The cost figures are based strictly on the extrapolation of the pilot plant experimental data taken at a flow rate

TABLE 16

COST ESTIMATE FOR 100,000 GPD PLANT

EQUIPMENT AND CONSTRUCTION COST	
Column 7 ft diameter, with valves and auxiliary equipment	$ 138,000
Resin, 720 cu ft*	6,624
Site preparation	2,376
Sub-total	147,000
Erection cost and start-up 15%	22,000
Total plant cost	$ 169,000
FIXED CHARGES	
Capital cost, 6% per year	$ 10,000
Depreciation, 30 years	5,633
Insurance, 1% of plant	1,690
Sub-total	17,323
Administrative expenses 10%	1,732
Total fixed charges	$ 19,055
OPERATING COST	Per 1,000 gal
Resin replacement in 4 years	$ 0.055
Electricity, variable	0.010
Lime loss at $20/ton	0.010
Sub-total	0.075
Fixed charges	0.190
Waste purification cost	$ 0.265

TABLE 16 (Cont'd.)

POSSIBLE CREDIT	Per 1,000 gal
Reclaimed water	$ 0.30
Reclaimed salt at $20/ton	0.20
Sub-total	0.50
Possible profit	$ 0.24

of 4.0 gpm, which corresponds to 5.1 gpm/sq ft. No charge is made for labor, since it is felt that food processor or a municipal sewage treatment plant can easily assign the task to a paid employee. This additional assignment would not take much time because the treatment unit is fully automated and recording devices can be placed remotely. The cost estimate is for a 100,000 gpd plant at 2,500 ppm influent NaCl. The cost estimate applies to one set of circumstances and is, therefore, subject to variation. Among these circumstances are capital cost, local price and/or need for reclaimed water, assessment of salt value, accounting principles, etc.

SECTION VI

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We are indebted to Kenneth A. Dostal of the Pacific Northwest Water Laboratory of WQO-EPA for his many helpful suggestions and guidance in the preparation of reports.

The following members of the staff of the NCA Berkeley Laboratory made significant contributions to the obtaining and reporting of results:

Nabil L. Yacoub, Edwin S. Doyle, Stuart Judd

Walter A. Mercer
Grant Director

Jack W. Ralls
Project Director

SECTICN VII

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SECTION VIII

PATENTS AND PUBLICATIONS

The process technology used in the Aqua-Ion system is defined by U.S. Patent 3,073,725 (issued in 1963 to K. Popper and V. Slamecka). The Aqua-Ion Corporation has established the following policy position with respect to utilization of their process technology for food processing brine treatment.

"Our patents are process patents and do not cover equipment; they cover merely the manner in which to handle a given type of material. Thus, we cannot collect equipment royalties; any royalties coming to us will have to be derived from use. Any royalties we will ask for will be based on savings the process will give the user beyond such expenses as the user may have with waste disposal. Typically, one may deal with a situation where the cannery pays $0.10 sewerage charges, $0.10 a thousand gallons for water and where using our system it will return $0.17 worth of salt to process. According to our preliminary calculations, the waste purification cost will be $0.17. Thus we see a saving of $0.20, and we would like to negotiate a reasonable royalty on that."

No publications have resulted from work done in the project to date. The first public disclosure of the total project result was at the Second National Food Processing Waste Symposium, Denver, Colorado, March 23 - 26 1971.

1 Accession Number	2 Subject Field & Group	
	05 D	**SELECTED WATER RESOURCES ABSTRACTS** INPUT TRANSACTION FORM

5 *Organization*

National Canners Association, Berkeley, California
Western Research Laboratory

6 *Title*

REDUCTION OF SALT CONTENT OF FOOD PROCESSING LIQUID WASTE EFFLUENT

10 *Author(s)*

Mercer, Walter A.

Ralls, Jack W.

16 *Project Designation*

EPA, WQO Project 12060 DXL

21 *Note*

22 *Citation*

23 *Descriptors (Starred First)*

* Brine Desalination, Food Processing, Ion Exchange Treatment, Salt Removal, Olive Processing

25 *Identifiers (Starred First)*

* Brine Treatment, Food Processing Brines

27 *Abstract* Olive processing brines containing 0.05 to 0.7 percent sodium chloride were passed through a mixed bed of cation and anion exchange resins. The effect of influent composition on the composition of effluent from the ion exchange unit was investigated, using a range of influent pH, salt content, and C.O.D. levels. The unit was operated at sodium chloride levels of 500 to 7,000 ppm with random pH and C.O.D. levels. The highest removal of sodium chloride (94 percent) was obtained at a level of 2,700 ppm sodium chloride in the influent. With pH and C.O.D. held constant, the salt content of the influent was varied between 600 and 6,000 ppm. The effluent sodium chloride content was approximately 150 ppm at 600, 1,000 and 2,700 ppm and was 790 ppm at 6,000 ppm influent concentration.

The resins were regenerated using a solution of calcium hydroxide. To establish the maximum salt concentration attainable in the regenerant effluent, the regenerant was repeatedly recycled through the resin bed. The sodium chloride content of recycled regenerant solutions was increased 40 percent over the influent brine level, and evidence was obtained that at least a ten-fold increase was possible.

The cost of desalination of dilute food processing brines by this ion-exchange treatment was estimated at $0.26 per 1,000 gallons of influent. (Ralls - NCA)

Abstractor	Institution
Jack W. Ralls	National Canners Association