## LABORATORY EVALUATION OF COAGULATION-PRECIPITATION AND ULTRAFILTRATION FOR REGENERATION OF STORAGE BRINES

One approach to reduction of salt in pickle wastewaters is regeneration and reuse of salt brines within the manufacturing process. As previously noted there are two major sources of high salt wastes: (1) the used (spent) brine from tanking and storage, and (2) the processing waters resulting from washing and firming the salt stock prior to packing. Tankyard brines, which are currently discharged into the ground in most plants, are of two strengths (1) the "36-hr drain" of -7% salt from the smaller cucumbers, and (2) the storage brine of -16% salt.

### Coagulation-Precipitation

Coagulation-precipitation as a means of brine regeneration has been investigated by Geisman and Henne (1973). These investigators, basing their work on earlier work by Popper et al. (1967), used chemical precipitation followed by clarification (filtration) and activated carbon treatment. Of the chemicals tested, NaOH was found to be the most economical and effective. Brines of $50^0$ and $70^0$ salometer were treated by adding NaOH to a pH of 11.0, then filtered through cotton precoated with diatomaceous earth. Filter effluent was passed through an activated carbon bed, then neutralized with HCl. Geisman and Henne reported COD reductions of 50-97%, but since COD data are not included in the tabulated data, it is not possible to determine volumes used or the step in the process responsible for the reduction. When the process was tested on commercial scale, the high costs of filtering and activated carbon treatment resulted in omission of these steps. Settling for 48 hr, followed by removal and neutralization of the clear supernatant, was substituted.

Pickles made with brine regenerated by this method were found to be comparable in quality to those made with freshly made brine.

Geisman and Henne estimated the cost for treating brines by this method at $1450 for brine for 100,000 bushels of cucumbers. This cost would be counterbalanced by a savings of $3100 for salt needed for that amount of brine.

Palnitkar and McFeeters (1974) treated spent brines with alkali, using the method of Geisman and Henne. Their results were similar to those found in our work, i.e., little or no organic material was removed and only small amounts of Kjeldahl nitrogen were removed. They fermented cucumbers (size 3B) in untreated brine, fresh brine, base treated brine, and heat treated brine, and found that there was no difference in color, odor, and texture.

## Discussion and Conclusions

In general, as expected, wastewaters from cucumber pickling operations are characterized by high chloride content, high oxygen demand, low pH, and high total and suspended solids. Nutrient concentrations, especially Kjeld-N, are also appreciable. The 36-hour drain from small cucumbers contains about 0.6 lb NaCl/gal and also contains appreciable organic carbon and other components leached from the cucumbers. The spent tankyard brines contain high concentrations of salt (1.0-1.6 lb NaCl/gal) and also, on the average, 3400 mg/l of organic carbon, 330 mg/l of suspended solids, 730 mg/l of total Kjeld-N, 90 mg/l of phosphorus, and 2300 mg/l of acidity (as $CaCO_3$). The pH falls between 3 and 4. These brines have a high pollutional pa tential and are much more concentrated than domestic sewage.

Desalting (processing) wastewaters are also typically of low pH and relatively high chloride concentrations. In the first desalting water chloride levels are about 40 gm Cl/l. Organic carbon levels are high and in general the more finely divided the product, the higher the TOC as well as the Kjeld-N and phosphorus levels. Apparently, the greater the surface area exposed to the processing water, the greater the loss of soluble components and fragments of cucumber tissue.

Water requirements per unit of cucumbers handled vary widely within each unit process. Part of the variation can be attributed to leakage, overflow, or failure to close valves during times when the unit is not in operation. The water use studies indicate that 40-90 % of the water currently used is unnecessary. Reduction of unnecessary water use would lower the hydraulic loading on the wastewater treatment system, increasing the detention time, and would also reduce cost of water.

The potential for reuse of pasteurizer water in cleanup or other areas should be investigated. Alternatively, to reduce loading on the wastewater treatment system the possibility of discharging the relatively clean pasteurizer water to the municipal system should be investigated by plants not currently doing so.

Approximately 40-50 % of each year's cucumber crop is fresh-packed rather than brined, and fresh-pack operations generally predominate during the period from May-August. However, the plant wastewater continues to be characterized by high salt and organic carbon levels, since during this time 50-60 % of the cucumbers are brined. Brining is associated with intensive tankyard activity, including drainage of 36-hour brines from the smaller cucumbers. Salt spillage is also most apt to occur at this time. Loss of brines by overflow during rainfall and by leakage also occurs. With perimeter drainage systems, all wastewaters from the tankyard area will be discharged to become a part of the overall plant wastewater. Therefore, it is not surprising that highsolids and chloride levels are found year-round at plants with perimeter systems.

Because of the highly pollutional nature of tankyard brines the present widespread practices of discharging these brines untreated onto the tankyard should be questioned. In addition, the potential of chloride contamination of groundwater by tankyard runoff or by seepage from unlined wastewater treatment ponds should be investigated.

Repetitive recycling experiments indicated that brine could be recycled at least 5 times with no effect on product quality, even though there was some buildup of organics. Their work also indicated a significant reduction in bloater content in pickles fermented in spent brine.

Laboratory studies conducted by Bell (personal communication, 1972) indicated that coagulation-precipitation of brine with lime and NaOH at pH 11 essentially eliminated softening enzyme activity, either by irreversible denaturation of the enzyme or by its physical removal with the sludge.

Since high pH coagulation-precipitation appeared to eliminate the softening enzyme, laboratory studies were conducted on-site at Plant A and at the UNC Wastewater Research Center to estimate amount of chemicals required for regeneration of brines by this method. A variety of storage brines from different sizes of cucumbers, as well as from other vegetables, was examined to determine if the brines differed significantly in their requirements.

A list of tanks, contents, and dates of filling was obtained from the yard foreman, and representative tanks were chosen for sampling. Samples were removed from a vertical sampling channel located in each tank which allows sampling at all depths.

To 1-L aliquots of each brine, 0.1% (1 gm) of hydrated lime [$Ca(OH)_2$; purified grade] was added during rapid mixing with a magnetic stirrer. pH was monitored with a pH meter (Leeds and Northrup, 7400-A 2 Series).

pH was recorded after lime addition. pH was then raised toll by addition of 5% NaOH solution (prepared by diluting commercial NaOH solution, 50% concentration, commonly purchased by pickle plants). After 5 min mixing during which floc formed, the brine was transferred to a 1-L graduate cylinder and allowed to settle for 30 min. Then, sludge volume was noted and a portion (300 ml)of supernatant was decanted to a 500 ml beaker (Pyrex) and titrated with acetic acid, 6.5% (prepared by diluting commercial grade acetic acid , 13% concentration) to pH 7.0. Alkali and acid requirements for different brines are indicated in Table 31.

Samples of untreated and treated brine were analyzed for TOC, solids, N forms, total phosphorus, and Cl . Results are shown in Table 32. As expected, phosphorus content was decreased and chloride content was unaffected. No appreciable amount of organic carbon was removed, indicating that the organic carbon is primarily in soluble form. While a visible improvement in overall clarity of the brine was achieved, there was no significant change in suspended solids levels. Apparently there was only a qualitative difference, possibly due to substitution for some of the solids initially present by a fine light chemical floc.

The results show a wide variation in buffer capacity among the various types of storage brines. Extremes generally were found in vegetables *was* other than cucumbers. Onion brine was especially low in buffer capacity, and the addition of the lime was sufficient to raise pH to 11.6 and effect good coagulation. Of course, little sludge was produced. At the other

TABLE 31. BASE OR ACID REQUIRED FOR SPENT BRINE COAGULATION-PRECIPITATION

| STOCK | pH Initial | pH After 0.1% Lime Addition | 5% NaOH to pH 11.5 (ml/l or gal/1,000 gal) | Sludge (% volume) | 6.5% Acetic Acid to (pH) (ml/l or gal/1,000 gal) |
|---|---|---|---|---|---|
| Cucumbers, field run, fall | 3.25 | 3.70 | 53.4 | 38% | 43.6 (6.8) |
| Cucumbers, field run, spring | 3.60 | 4.70 | 29.7 | 50% | 37.6 (6.8) |
| Cucumbers, 1B, spring | 3.40 | 8.90 | 14.6 | 26% | 27.3 (5.8) |
| Cucumbers, 2A, spring | 3.40 | 4.35 | 24.8 | 33% | 27.3 (6.7) |
| Cucumbers, 3, fall | 3.55 | 3.95 | 43.3 | 46.5% | 41.6 (5.9) |
| Cucumbers, 4, fall | 3.50 | 4.20 | 20.8 | no data | 28.3 (6.8) |
| Cucumber relish, spring | 3.30 | 5.10 | 19.8 | 47.5% | 20.3 (6.3) |
| Cucumber relish, fall | 3.30 | 3.90 | 46.4 | 49% | 39.6 (6.8) |
| Cauliflower | 3.90 | 6.10 | 51.9 | 30% | 77.9 (6.95) |
| Pepper | 4.00 | 8.80 | 59.7 | no precipitation after 20 min. | - - - - |
| Onion | 4.10 | 11.60 | ---- | 5% | 35.5 (4.6) |

TABLE 32. TANK-YARD BRINE SAMPLES BEFORE AND AFTER COAGULATION-PRECIPITATION

| PRODUCT | TANK * NO. | TOC | SS | $NH_4$-N | Kjeld-N | TP | PH |
|---|---|---|---|---|---|---|---|
| | | mg/l | | | | | |
| Cucumbers, field run, fall | 18-l i | 5800 | 388 | 275 | 500 | 87.5 | 3.3 |
| | f | 5500 | 437 | 250 | 400 | 10.1 | 11.8 |
| Cucumbers, field run, spring | 30-4 i | 3700 | 451 | 200 | 300 | 85.0 | 3.7 |
| | f | 3300 | 342 | 175 | 275 | 5.6 | 11.9 |
| Cucumbers, 1B spring | 45-14i | 1400 | 460 | 200 | 225 | 38.5 | 3.5 |
| | f | 1400 | 482 | 113 | 163 | 4.5 | 11.7 |
| Cucumbers, 2A, spring | 24-121 | 2800 | 288 | 175 | 250 | 56.5 | 3.4 |
| | f | 2800 | 530 | 150 | 225 | 7.8 | 11.6 |
| Cucumbers, 3, fall | 23-16i | 4700 | 260 | 300 | 425 | 83.5 | 3.6 |
| | f | 4800 | 340 | 275 | 425 | 6.6 | 11.7 |
| Cucumbers, 4, fall | 16-18i | 3500 | 343 | 225 | 363 | 152 | 3.5 |
| | f | 3400 | 348 | 213 | 338 | 6.0 | 11.4 |
| Cucumber relish, spring | l0-13i | 1300 | 259 | 100 | 150 | 28.0 | 3.2 |
| | f | 1200 | 408 | 88 | 138 | 4.9 | 11.5 |
| Cucumber relish, fall | 24-14i | 5000 | 337 | 325 | 500 | 93.0 | 3.5 |
| | f | 4700 | 321 | 275 | 450 | 6.2 | 11 8 |
| Cauliflower | 28-17i | 7700 | 447 | 350 | 950 | 155 | 4.1 |
| | f | 6900 | 434 | 375 | 825 | 5-3 | 11.7 |
| Pepper | 25-7 i | 6900 | 262 | 125 | 350 | 80.0 | 4.3 |
| | f | | | | | | |
| Onion | l-1Oi | 0 | 131 | 40 | 45 | 8.9 | 4.1 |
| | f | 0 | 444 | 20 | 30 | 1.5 | 11.9 |

* i= initial, untreated sample; f= final, treated sample -

extreme, pepper brine had a high buffer capacity and exhibited little or no settling after 30 min settling time,

Cucumber brines exhibited a range of buffer capacities, and there was no apparent correlation of buffer capacity with size or season. On the average, approximately 0.3% (vol/vol) of caustic soda solution (50% NaOH) was required to raise the pH to 11.5. To neutralize the supernatant, approximately 1.7% (vol/vol) of acetic acid solution(l3%) was required.

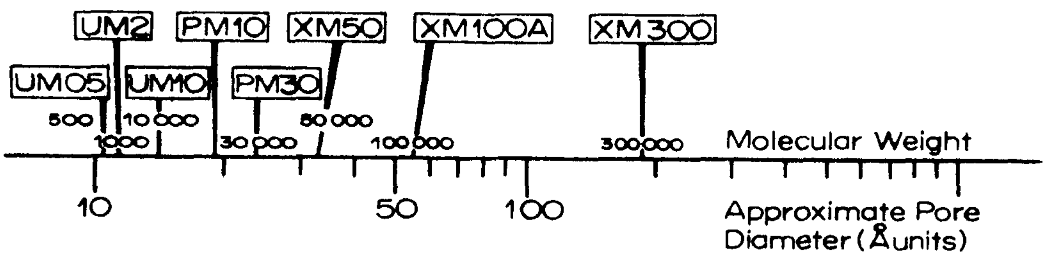


FIGURE 3. RETENTION OF ULTRAFILTERS
Retention depends on molecular size and configuration. MW cut-off shown applies to protein. (From Amicon Corp., 1972)

## Ultrafiltration

Molecular filtration (ultrafiltration) is a relatively new process for removing large molecular weight (MW) compounds from aqueous solutions. By selection of a membrane of suitable pore-size, compounds of a specific MW range can be retained. While ultrafiltration has been used to recover valuable components from milk and other wastes, no information has been published on the possibility of treating pickle brines by this method. Since enzymes are large macromolecules, generally with molecular weights of 100,000 or more, it was anticipated that softening enzyme would be easily removed with a relatively large pore size. The bulk of the soluble organic material in pickle brines has not been identified. It was hoped, however, that with suitable membranes substantial amounts of this organic carbon could be removed.

## A. Materials and Methods

### 1. Membranes

#### a. Type

Amicon Diaflo[R] ultrafilters were employed. This type of filter consists of an anisotropic polymeric membrane on a porous substructure. Characteristics of different ultrafilters and microporous filters are shown in Figure 3. For these studies the following membrane sizes were employed: XM 300, XM lOOA, XM 50, PM 30, PM 10, and UM 2. The number of each type of filter indicates its porosity in terms of molecular weight, i.e., XM 300 has a mean pore size of 300,000 MW; XM, of 50,000 MW. As noted in Amicon literature, since indicated pore size is a mean value, for maximal retention a cut-off size well below MW of the solute to be retained is generally chosen.

#### b. Membrane Preparation and Storage

Ultrafilters of the XM series are supplied ready for use. Filters in the PM and UM series have a glycerin film to prevent drying out; these filters were prepared by rinsing in distilled water for 1 hr with one change of water prior to use. Filters could be stored by refrigeration in 10% ethanol. In most instances, however, new filters were used to make results more comparable.

#### C. Flux

During serial filtration experiments rate of ultrafiltration was determined for each of the membranes. This was done by collecting filtrate in 10 ml graduate cylinders using a stopwatch to measure time required for production of 5 ml aliquots. By use of two stopwatches, flow rate over time could be determined.

### 2. Cell

For ultrafiltration studies a stirred cell (Amicon) was employed. Cell capacity is 50 ml of feed solution, but larger volumes can be filtered continuously by coupling a feed reservoir between the cell and the pressurized gas tank. Magnetic stirring in the cell minimizes concentration polarization. To prevent heating of cell contents, air from a laboratory air line was used to cool the magnetic stirrer.

### 3. Pretreatment of Sample

Preliminary experiments indicated that unless gross suspended solids were removed from the feed, ultrafiltration rates were extremely slow. Therefore, feed samples were pretreated by vacuum filtration through a membrane filter (5.0 um pore size, Metricel GA-l, Gelman).

4. Temperature

All filtrations were performed in a constant temperature room maintained at 21 C. Samples stored by refrigeration were allowed to reach room temperature before filtration.

5. Pressure

Pressure for the cell was provided with pressurized nitrogen gas and regulated by the pressure valve on the tank. A pressure of 30 psi was used for XM 300, XM lOOA, and XM 50 membranes; 60 psi, for smaller pore-sized membranes.

6. Experimental Approach

Experiments involved two approaches to ultrafiltration: parallel and serial. In the former, the feed sample was subdivided into identical aliquots, each of which was passed through a different size of filter. In the latter, the feed was passed through a large-pore filter, the filtrate serving as feed for the next finer filter, and so on. In the second procedure it was difficult to filter enough through the initial membranes to provide sufficient volume for feed and analyses throughout the filter series.

7. Analytical Procedures

Pickle brine samples present difficulties in analysis due to corrosiveness and to interference of Cl in many analytical procedures. In many cases analytical methods required modification to compensate for these characteristics.

a. Chloride

Chloride concentrations were measured chemically or electrometrically. In earlier work and in all of the coagulation-precipitation and ultrafiltration studies Cl was determined using the high concentration modification of the mercuric nitrate method (standard Methods,1971 ). Even with this modification, the high salinity of spent brines required considerable (x 50) dilution of samples.

b. COD

Chemical oxygen demand (COD) was measured using the procedure recommended for wastewaters (Standard Methods, 1971.). To compensate for Cl interference, mercuric sulfate was added in the proportions indicated.

C. TOC

Total organic carbon (TOC) analysis generally offers a rapid means of measuring organic carbon in wastewater. However, problems were encountered with brine samples due to their high Cl content. With the instrument available (Model 915 TOC Analyzer, Beckman Instruments), brine caused corrosion of the combustion chamber and the adjacent stainless steel tubing. Discussions with Beckman personnel indicated that there was no way to modify the instrument so that it could handle undiluted spent brines: Therefore, samples were diluted sufficiently to lower Cl concentration to <l000 mg/l. This resulted in unavoidable loss of some accuracy, especially in instances in which Cl concentration was high in proportion to organic carbon concentration.

d. Pectinase Activity

To assure high levels of enzyme activity in the untreated brine, commercial pectinase was added prior to filtration. These high levels made it possible to magnify any reductions in enzyme activity. Pectinase was obtained from the USDA Food Fermentation Laboratory in Raleigh.

All analyses of pectinase activity were performed by Ms. Horney at the USDA Laboratory under the direction of T. A. Bell who developed the analytical method (Bell et al, 1955). In brief, the method is based on the ability of pectinase to break down sodium polypectate and thus reduce its viscosity. Since salt interferes with the test, the sample must be dialyzed prior to analysis.

B. Results

Preliminary tests were conducted by filtering 50 ml aliquots of 36-hr brine through the largest filters (XM 300, XM lOOA, and XM 50). Chloride and COD concentrations were determined on the untreated brine and the filtrate. Pectinase activity was measured in untreated brine, filtrate, and concentrate. Results of these tests are shown in Table 33.

That pectinase was being removed by ultrafiltration is indicated by a decrease in filtrate activity along with increased concentrate activity. As anticipated, salt concentrations remained constant, within expected experimental error. Note that the amount of COD removed was approximately the same regardless of filter size. This removal was due primarily to removal of suspended solids rather than to removal of soluble organics.

Results from a serial filtration of 36-hr brine through the XM 300, XM lOOA, and XM 50 filters are shown in Table 34. Again, the salt concentrations were found to remain nearly constant throughout and there were no marked changes in COD although some removal was observed as indicated primarily by increased values in concentrate samples. The low pectinase activities throughout were due to enzyme breakdown during storage of the stock solution. For subsequent tests fresh solutions were made. However, the problem of whether decreases in enzyme activities could be attributed to effects of ultrafiltration or were merely a function of time needed to be resolved.

To resolve this problem, a fresh batch of brine with added pectinase was allowed to stand at room temperature with no preservative (toluene)

TABLE 33. EFFECT OF PARALLEL ULTRAFILTRATION ON 36-HR BRINE

| Sample | Cl mg/l | COD mg/l | Pectinase Activity (units) |
|---|---|---|---|
| | Parameter | | |
| Untreated | 54,300 | 3,700 | 856 |
| XM 300, filtrate | 53,000 | 2,400 | {570<br>516 |
| XM 100A, filtrate | 54,800 | 2,400 | {516<br>338 |
| XM 100A, concentrate | ------ | ----- | 1158 |
| XM 50, filtrate | 52,400 | 2,300 | {161<br>246 |
| XM 50, concentrate | ------ | ----- | 1393 |

TABLE 34. EFFECT OF SERIAL ULTRAFILTRATION (XM 300 → XM 50) ON 36-HOUR BRINE

| | Filtrate | | | Concentrate | | |
|---|---|---|---|---|---|---|
| Sample | Cl mg/l | COD mg/l | Pectinase units | Cl mg/l | COD mg/l | Pectinase units |
| Untreated | 25,700 | 16,200 | 39 | | | |
| XM 300 | 26,100 | 15,700 | 34 | --- | 18,800 | 110 |
| | 26,100 | 16,100 | 7 | | | |
| | 26,300 | 16,000 | 14 | | | |
| XM 100 A | 25,600 | 15,100 | 11 | 25,500 | 16,100 | 11 |
| | 25,400 | 15,400 | 14 | | | |
| | 25,000 | 15,500 | 13 | | | |
| | 25,500 | 15,600 | 9 | | | |
| XM 50 | 25,600 | 15,100 | 5 | 24,700 | 15,400 | 37 |
| | 24,500 | 15,000 | 8 | | | |

added. At intervals samples were taken, preserved with toluene, and refrigerated. Enzyme activity levels are shown in Table 35.

TABLE 35. EFFECT OF STANDING ON PECTINASE ACTIVITY

| Time,hr | Pectinase Activity, units |
|---|---|
| 0.0 | 650 |
| 2.5 | 957 |
| 4.0 | 800 |
| 6.0 | 1140 |
| 12.0 | 828 |

The reason for the low level of activity in the fresh sample is not known. More important are the relatively constant levels at the later times, indicating that the enzyme does not break down within a few hours. It also points out the relatively wide variation that may occur within one enzyme test. Therefore, actual reduction would be indicated by larger differences than those observed above.

Serial filtration was repeated with smaller pore-sized ultrafilters. Results are shown in Table 36 and in Figure 4. Again, the COD was affected very little by ultrafiltration. Enzyme activity was substantially reduced by ultrafilters smaller than XM 50.

Since serial filtration necessitates filtering larger amounts of brine through the larger-sized filters, the different filter types could better be compared by filtering equal amounts of untreated brine. Again, pectinase was added and the sample was pretreated by filtration through a 5.0 u membrane filter. Results of such tests are shown in Table 37 and in Figure 5. Only enzyme activity was monitored since it had been demonstrated repeatedly that no significant removal of COD could be achieved. It is apparent that pectinase is removed significantly by ultrafilters PM 30 and smaller.

Flux of filtrate through the various sized ultrafilters during serial filtration is shown in Figure 6. Originally experiments were designed to use the same pressure (30 psi) for each filter, but filtration rates became so slow that higher pressure was used (60 psi). It should also be noted that solute concentrations in the feed solutions of the smaller pore-sized ultrafilters would be decreasing continually. While this does not make the flux performance for each filter as comparable as if the same feed solutions were used, common operating procedures may use 20 or more different sizes of filters in series. These results should show optimum flux rates for brine solutions at the pressures shown.

TABLE 36. EFFECT OF SERIAL FILTRATION (5.0 μ → UM 2) ON 36 HOUR BRINE

| Filter | Filtrate | | Concentrate | |
|---|---|---|---|---|
| | COD mg/l | Pectinase Activity | COD mg/l | Pectinase Activity |
| Untreated | 3350 | 1,446 | | |
| 5.0 μ | 3330 | 1,510 | | |
| XM 300 | 3270 | 1,350 | 3330 | too high to measure |
| XM 100A | 2800 | 1,330 | 3000 | 1,730 |
| XM 50 | 2700 | 950 | 2800 | 3,100 |
| PM 30 | 2800 | 236 | | |
| PM 10 | 2700 | 65 | 2900 | 310 |
| UM 2 | 2500 | 10 | 3200 | 150 |

TABLE 37. EFFECT OF ULTRAFILTRATION (2000-10,000 MW PORES) ON PECTINASE ACTIVITY OF BRINE

| Filter | Pectinase Activity (Units) | |
|---|---|---|
| | Filtrate | Concentrate |
| Untreated | 3028<br>2927 | |
| 5.0 μ | 2800<br>2560<br>2509 | |
| XM 100A | 2625<br>1936 | 3229<br>3257 |
| XM 50 | 990 | 4793 |
| PM 30 | 28 | 4393 |
| PM 10 | 16 | 4742 |
| UM 2 | 0 | 4997 |

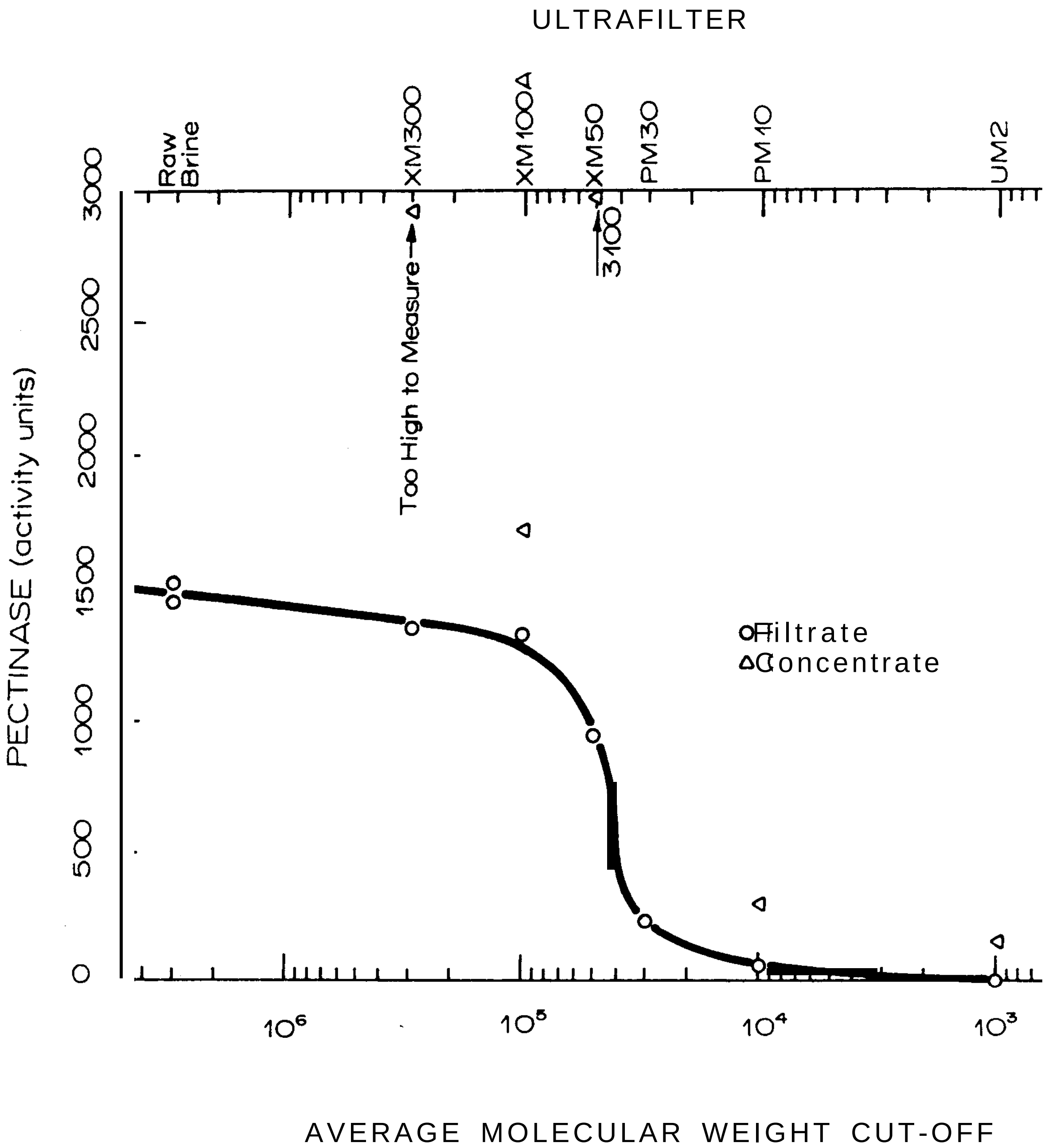


FIGURE 4. EFFECT OF SERIAL ULTRAFILTRATION ON PECTINASE ACTIVITY IN 36-HR BRINE

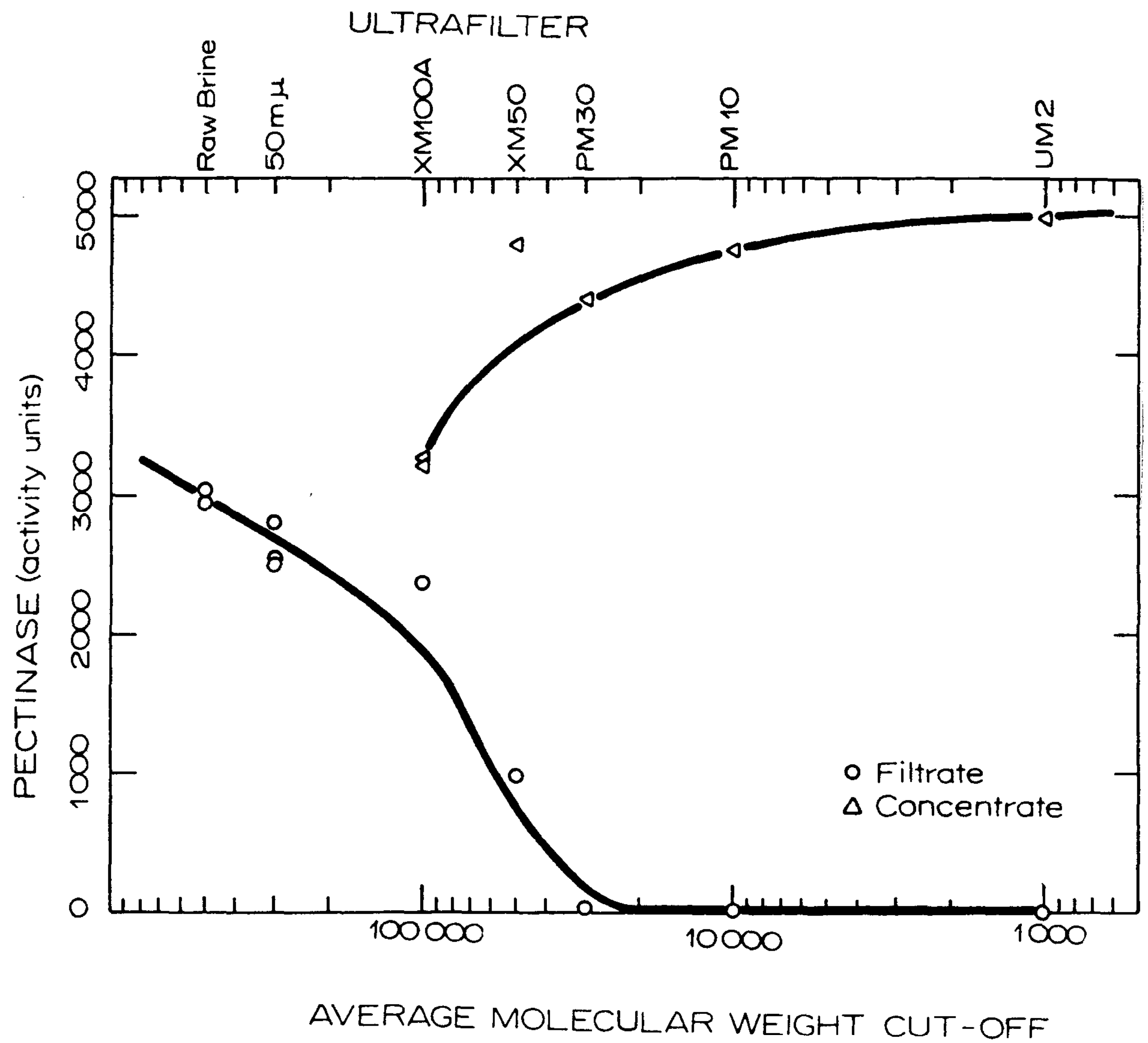


FIGURE 5. EFFECT OF ULTRAFILTRATION ON PECTINASE ACTIVITY IN SPENT BRINE

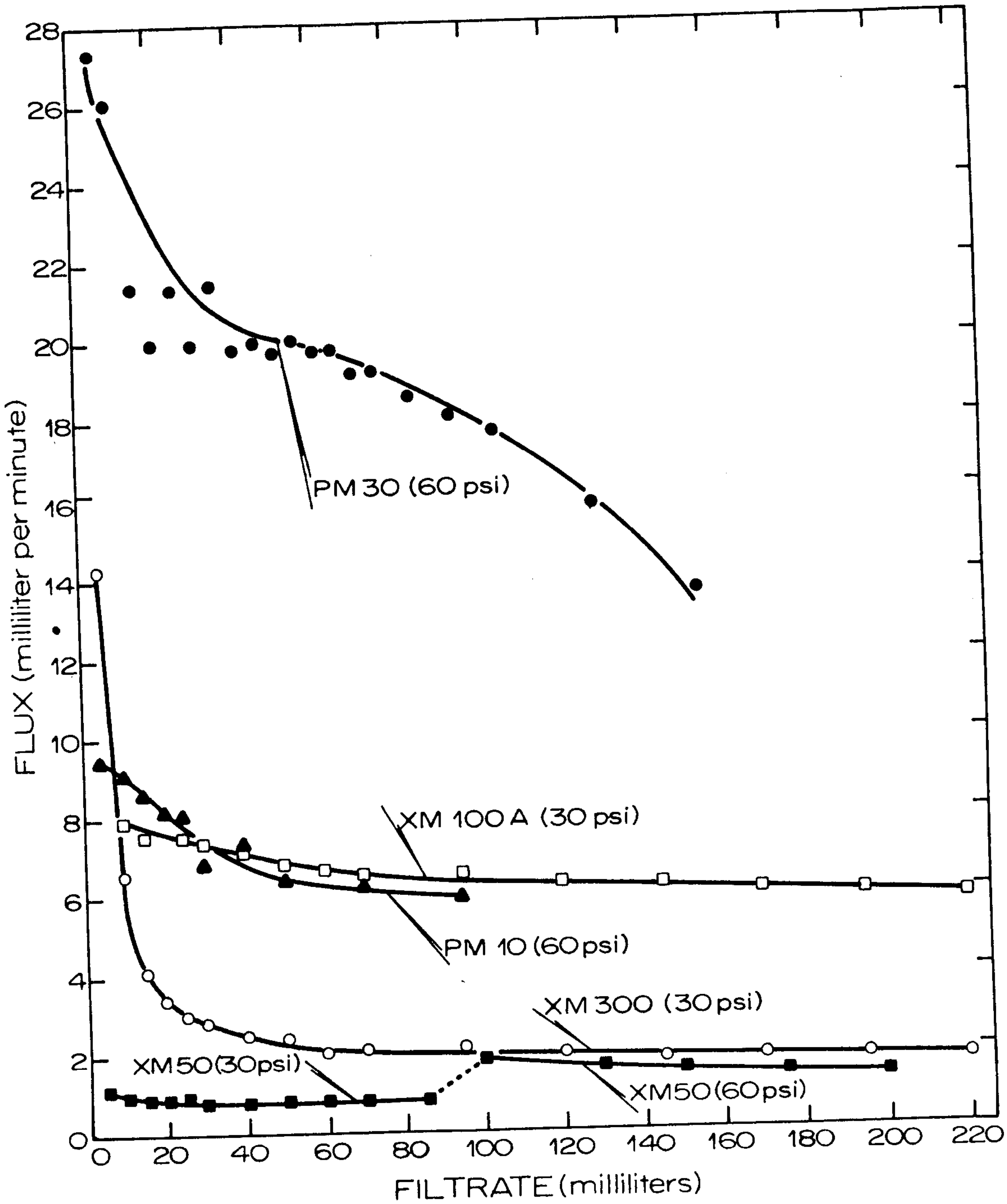


FIGURE 6. FLUX DURING SERIAL ULTRAFILTRATION

## Discussion and Conclusions

Previous studies by Bell had shown that coagulation-precipitation is an effective means of removing pectinase activity from spent brines. Ultrafiltration results from this study show that it too is an effective means of removing pectinase activity. Neither treatment substantially reduces the COD of the brine,

Further comparison of the two methods should be made in terms of economics. Economic considerations were foremost in Geisman's (1973) recommendation of coagulation-precipitation over other methods of brine regeneration. Inflation and fuel shortages of the past few years have rendered cost estimates made in previous studies outdated. While the scope of this study does not allow detailed cost comparisons, factors to be considered for both types of treatment can be discussed.

Treatment by coagulation-precipitation requires large quantities of caustic soda and glacial acetic acid, both of which have become more expensive and at some times unavailable immediately upon request. Chemical costs depend on quantities purchased and are cheapest by tank loads of 20-23 tons. Prices given by local chemical supply companies range from $145-160 per ton for caustic soda; for acetic acid, from $300-340 per ton. In both cases, costs were based on tank load purchases. Cost of storage would have to be compared with increased purchase costs for lower volumes per order. Freight and handling would also require consideration.

Costs of actual treatment (assuming batch type reactors) would include a mixing chamber and settling tank, pH monitoring equipment, and chemical feed equipment. The large quantities of sludge generated would require additional handling; possibly the sludge could be discharged into the aerated lagoon wastewater treatment system currently used at most plants.

Ultrafiltration eliminates the expense of chemical purchase, transport, and storage, and also does not present the occupational hazards associated with handling strong acids and caustics, However, the initial costs of ultrafiltration units are high, as are the costs of replacing membrane components when they become damaged or become fouled beyond regeneration. Most waste treatment-operations utilizing ultrafiltration use thin channel or hollow fiber systems rather than plate-type membranes. These systems are reportedly more efficient and present less problems with clogging. Power costs are associated with ultrafiltration since a pressure gradient must be maintained across the membrane. The pressure to be maintained depends on the flux desired and on the membrane surface area. Often it is more economical to increase surface area than to increase pressure, but this would have to be studied to determine the optimum area and pressure for the optimum membrane pore size. From the results of this study, PM 10 size membranes appear to be the largest feasible.

Both types of brine treatment require storage facilities for spent brine after removal from brining vats prior to treatment, as well as storage of treated brine until reuse.

The question arises as to how well treated brine can be stored before reuse. Since COD remains high in the treated brines, unless the brines are stored aseptically there is a likelihood of bacterial or fungal growth and the possibility of causing off-flavors in cucumbers brined in the regenerated brine, Some companies have been reusing heat-treated brines and they report no deterioration in quality of product, but the possible build-up of small molecular weight organics over a period of years cannot be dismissed. If spent brine were stored and then treated before reuse, excessive microbial growth might cause problems in sanitation. On the other hand, if stored after treatment some microbial growth might necessitate re-treatment before reuse. One plant stores all salt as 100% saturated brine and uses no dry salt. Treated brine is recycled into the $100^0$ salometer holding tank and this high salt concentration evidently prevents any problems of microbial growth.

Recycling of brines does seem feasible for cucumber pickling operations. From the point of view of this study, ultrafiltration appears more favorable as it is simpler in terms of handling and personnel required, but it would be necessary for each plant to determine the most cost-effective method based on its own situation,

## PILOT-SCALE EVALUATION OF COAGULATION-PRECIPITATION FOR REGENERATION OF 36-HOUR AND SPENT BRINES

Two large-scale pilot studies were conducted at Mount Olive Pickle Plant. In the first study, 36-40 hour brine from small cucumbers was used; in the second study, spent brine. Objective of the experiments was to evaluate the feasibility of reuse of brine after treatment with lime and sodium hydroxide.

### REGENERATION OF 36-40 HOUR BRINE

Brine (36-40 hr) was collected from a commercial vat of No. 1 size cucumbers brined at 25" salometer (6.6% salt). This brine was used to re-pack cucumbers from the same commercial vat. For the pilot testing 60 gal plastic-lined metal drums with plastic "heads" were used.

Four types of treatment were employed, and control with new brine was included. Each test was run in duplicate, giving a total of 10 drums. The test drums were set up as shown in Table 38.

TABLE 38. EXPERIMENTAL DESIGN FOR EVALUATION OF COAGULATION-PRECIPITATION FOR REGENERATION OF 36-40 HOUR BRINE

| Drum No, | Brine Treatment |
|---|---|
| A-l, A-Z | New brine, 25" salometer |
| B-l, B-Z | Untreated 36-40 hr brine |
| C-l, c-z | Brine treated by high pH procedure, no pH adjustment |
| D-l, D-Z | Brine treated by high pH procedure, pH adjusted to 5.5 with acetic acid |
| E-l, E-Z | Brine treated by high pH procedure, pH adjusted to 5.5 with HCl |

Brines C, D, and E were prepared by the following procedures:

(1) Addition of 0.10% Ca(OH)2 while stirring
(2) Addition of 50% NaOH to a final pH of 11.9
(3) Quiescent settling for 2 hours
(4) Decanting of 45 gallons of clear brine to each of 6 test drums.

For C tanks, no further treatment was done. For D tanks, the pH was adjusted down to 5.5 with acetic acid; and for E tanks, the pH was adjusted down to 5.5 with HCl.

The test and control brines were used to repack the same cucumbers from which the 36-40 hr brine was drained. About 250 lbs of cucumbers were placed in each test drum. These cucumbers were at a low pH (around 5.3) and were still carrying a high level of bacterial flora.

Table 39 shows effect of the lime-NaOH treatment on the brine. Note that there was little or no effect on COD, indicating that most of the oxygen demand was associated with soluble components. An increase in Kjeldahl nitrogen was noted. This could possibly be due to solubilization of some of the nitrogen-containing organic materials. The major accomplishments of the procedure were (1) decrease in pectinase activity and, (2) decrease in total bacteria.

TABLE 39. TREATMENT OF 36-HOUR BRINE BY LIME-NaOH ADDITION

| Parameter | Before Treatment | After Treatment |
|---|---|---|
| Suspended Solids, mg/l | 390 | 289 |
| Total Solids, mg/l | 77,011 | 63,645 |
| COD, mg/l | 7,900 | 7,300 |
| Cl , mg/l | 39,500 | 31,500 |
| Kjeld-N, mg/l | 250 | 325 |
| $NH_4$-N, mg/l | 155 | 130 |
| Pectinase, units/ml | 16 | 0 |
| Cellulases, units/ml | 220 | ---- |
| Total Bacterial Count, no./ml | $6.8 \times 10^6$ | $9.6 \times 10^4$ |
| Acid Formers, no./ml | $5.0 \times 10^6$ | <10 |

The drums were then headed down and subjected to the usual salting schedule. Table 40 shows the progress of fermentation in the five sets of test drums. Note that within 3 days the pH in the "C" drums was almost as low as that in the control (A) drums. After 6 days the brines in the

TABLE 40. PROGRESS OF FERMENTATION IN NEW BRINES AND IN TREATED AND UNT 36-HOUR BRINES

| PARAMETER | TREATMENT | | ELAPSED TIME | | |
|---|---|---|---|---|---|
| | | | 3 hr | 3 days | 6 days |
| pH | A-1 | New | 5.2 | 3.8 | 3.7 |
| | 2 | | 5.3 | 3.7 | 3.7 |
| | B-1 | Untreated | 5.3 | 3.8 | 3.7 |
| | 2 | | 5.4 | 3.8 | 3.8 |
| | C-1 | Treated, pH 11 | 9.1 | 4.2 | 4.1 |
| | 2 | | 9.2 | 4.3 | 4.3 |
| | D-1 | Treated, pH 5.5 | 5.4 | 4.1 | 4.1 |
| | 2 | with $CH_3COOH$ | 5.4 | 4.1 | 4.2 |
| | E-1 | Treated, pH 5.5 | 5.4 | 3.7 | 3.7 |
| | 2 | with HCl | 5.7 | 3.8 | 3.8 |
| Sugar, % | A-1 | | 0.46 | 0.00 | 0.08 |
| | 2 | | 0.48 | 0.08 | 0.08 |
| | B-1 | | 0.61 | 0.08 | 0.08 |
| | 2 | | 0.65 | 0.08 | 0.08 |
| | C-1 | | 0.64 | 0.12 | 0.08 |
| | 2 | | 0.66 | 0.00 | 0.08 |
| | D-1 | | 0.64 | 0.08 | 0.08 |
| | 2 | | 0.63 | 0.08 | 0.08 |
| | E-1 | | 0.69 | 0.08 | 0.08 |
| | 2 | | 0.63 | 0.00 | 0.08 |
| Pectinase, units/ml | A-1 | | 3 | 0 | 0 |
| | 2 | | 0 | 0 | 0 |
| | B-1 | | 13 | 0 | 0 |
| | 2 | | 12 | 4 | 0 |
| | C-1 | | 0 | 1 | 0 |
| | 2 | | 0 | 0 | 0 |
| | D-1 | | 3 | 4 | 0 |
| | 2 | | 6 | 0 | 0 |
| | E-1 | | 7 | 0 | 0 |
| | 2 | | 11 | 0 | 0 |
| Kjeld-N, mg/l | A-1 | | - | 725 | 825 |
| | 2 | | - | 800 | 900 |
| | B-1 | | - | 950 | 1050 |
| | 2 | | - | 900 | 850 |
| | C-1 | | - | 875 | 1000 |
| | 2 | | - | 950 | 1025 |
| | D-1 | | - | 975 | 1125 |
| | 2 | | - | 1000 | 1100 |
| | E-1 | | - | 975 | 1075 |
| | 2 | | - | 800 | 800 |

TABLE 40 (continued)

| PARAMETER | TREATMENT | ELAPSED TIME 3 hr | 3 days | 6 days |
|---|---|---|---|---|
| COD, g/l | A-1 | - | 15.5 | 12.7 |
| | 2 | - | 16.2 | 12.4 |
| | B-1 | - | 17.9 | 14.9 |
| | 2 | - | 18.2 | 14.6 |
| | C-1 | - | 19.3 | 15.7 |
| | 2 | - | 18.3 | 15.9 |
| | D-1 | - | 20.2 | 17.3 |
| | 2 | - | 19.3 | 18.0 |
| | E-1 | - | 15.2 | 16.8 |
| | 2 | - | 14.0 | 17.5 |

TABLE 41. QUALITY OF BRINESTOCK FERMENTED IN NEW, TREATED, AND UNTREATED 36-HOUR BRINES

| Treatment | | Pressure Test, Units (av. of 10 cucumbers)* | Presence of Bloaters (40 cucumbers tested) |
|---|---|---|---|
| A-1 | New brine | 16.7 | 0 |
| 2 | | 16.7 | 0 |
| B-1 | Untreated | 16.0 | 0 |
| 2 | | 15.8 | 0 |
| C-1 | Treated, pH 11 | 16.7 | 5 |
| 2 | | 17.1 | 0 |
| D-1 | Treated, pH 5.5 | 17.1 | 0 |
| 2 | with $CH_3COOH$ | 17.3 | 0 |
| E-1 | Treated, pH 5.5 | 16.2 | 0 |
| 2 | with HCl | 17.7 | 0 |

*Cucumber size: $\frac{15}{16}$"; 36-hr cucumbers drained and brine replaced as indicated; stock tested after 18 days.

TABLE 42. EVALUATION OF CUCUMBER PICKLES BRINED IN NEW, UNTREATED, AND RECYCLED BRINES.

| Type | | Type of Brine | Appearance | Flavor | | Texture | Overall |
|---|---|---|---|---|---|---|---|
| | | | | Odor | Taste | | Acceptability |
| Sweet | A | New brine, 25° | 7.4 | 7.5 | 7.1 | 7.8 | 7.3 |
| | B | Untreated brine | 7.5 | 7.4 | 7.3 | 7.9 | 7.4 |
| | C | Floc, pH 11.5 | 7.2 | 7.2 | 7.2 | 7.2 | 6.8 |
| | D | Floc pH 5, acetic | 7.0 | 6.7 | 6.2 | 6.4 | 6.3 |
| | E | Floc, pH 5, HCl | 6.8 | 6.9 | 6.4 | 7.1 | 6.8 |
| Dill | A | New brine, 25° | 7.5 | 7.0 | 6.7 | 6.7 | 6.6 |
| | B | Untreated brine | 7.2 | 6.7 | 6.2 | 6.1 | 6.6 |
| | C | Floc, pH 11.5 | 7.0 | 6.4 | 5.2 | 6.0 | 5.3 |
| | D | Floc, pH 5, acetic | 7.3 | 7.3 | 7.3 | 7.4 | 7.2 |
| | E | Floc, pH 5, HCl | 7.8 | 7.3 | 7.6 | 6.8 | 7.2 |

Rating: 10, 9 = Excellent; 8, 7 = Good; 6, 5 = Fair; 4, 3 = Poor;
2, 1 = Barely or Not Acceptable

(Rating criteria devised by USDA Food Fermentation Laboratory) drums were similar in pH, sugar, pectinase content, and Kjeldahl nitrogen. The COD in all of the recycled brines was somewhat higher than in the control brine.

After 18 days the quality of the brinestock was evaluated (Table 41). There was little or no difference in quality as indicated by pressure tests. Bloater content was low in all drums with one exception, one of the "C" drums.

After storage, the brinestock was processed into dill or sweet pickles and a taste panel evaluated the quality of the pickles. As shown in Table 42, all the pickles were evaluated as fair to good in overall acceptability. The least acceptable overall rating was given to dill pickles which had been brined in recycled brine without pH adjustment.

## REGENERATION OF SPENT BRINE

In the second pilot study spent brine was regenerated by the lime-NaOH procedure and used to brine fresh cucumbers. Again, several types of treatment were employed and controls with new brine were included. The experimental design is shown in Table 43.

After the indicated treatments, the test brines were distributed to 10 drums, each containing 260 lb of #2 size fresh cucumbers. In Table 44 effect of lime-NaOH treatment on spent brine is shown. There was no significant difference in treated and untreated brine with the exception of the suspended solids, which decreased by almost 65% after treatment.

TABLE 43. EXPERIMENTAL DESIGN, EVALUATION OF COAGULATION-PRECIPITATION FOR REGENERATION OF SPENT BRINE

| Drum No. | Brine Treatment |
|---|---|
| F-l, F-2 | New brine, 30" Salometer |
| G-l, G-2 | Brine treated by high pH procedure, neutra--1ized to pH 6.0 with acetic acid, and diluted to 30" salometer |
| H-l, H-2 | New brine, 45" salometer |
| J-l, J-2 | Brine treated by high pH procedure, neutralized to pH 6.0 with acetic acid, and diluted to 45" salometer |
| K-l, K-2 | Brine treated by high pH procedure, no neutralization, diluted to 45" salometer |

TABLE 44. TREATMENT OF SPENT BRINE BY LIME-NaOH ADDITION

| Parameter | Before Treatment | After Treatment |
|---|---|---|
| Suspended Solids, mg/l | 599 | 209 |
| Total Solids, mg/l | 241,490 | 210,500 |
| COD, mg/l | 8,100 | 8,400 |
| Cl, g/l | 140 | 139 |
| Kjeld-N, mg/l | 300 | 275 |
| $NH_4$-N, mg/l | 250 | 220 |
| pH | 3.5 | 11.0 |

Brinestock quality was evaluated after 101 days (3 l/2 months). Results are shown in Table 45. In this experiment, quality of the cucumbers brined in recycled brine was equal to or better than those brined in new brines.

TABLE 45. QUALITY OF BRINESTOCK FERMENTED TN NEW BRINES AND IN TREATED SPENT BRINES

| Drums | Pressure Test, Units (av. of 10 cucumbers) | Presence of Bloaters % of 40 |
|---|---|---|
| F-l, F-2 | 14.6 | 23 |
| G-l, G-2 | 17.2 | 16 |
| H-l, H-2 | 15.7 | 14 |
| J-l, J-2 | 17.9 | 13 |

The progress of fermentation was also monitored, as shown in Table 47. As shown in Table 47, the pH in the recycled high pH brine dropped within 6 days to the level in the controls. Kjeldahl and ammonia N values were much higher initially in the recycled brines but after 6 days there were no consistent differences among treatments in content of these nitrogen forms.

TABLE 46. POTASSIUM CONTENT OF BRINES DURING FERMENTATION OF FRESH CUCUMBERS (2B and 3)

| Days Elapsed | Potassium, mg/l 30" Brine | Potassium, mg/l 45" Brine |
|---|---|---|
| 0 | 110 | 78 |
| 6 | 1250 | 1450 |
| | 1300 | 1550 |
| 22 | 1400 | 1440 |
| | 1600 | 1200 |

TABLE 47. PROGRESS OF FERMENTATION OF FRESH CUCUMBERS IN NEW BRINES AND IN TREATED SPENT BRINES

| Parameter | Treatment | | Elapsed Time 0 days | 6 days | 22 days |
|---|---|---|---|---|---|
| pH | F-1 | New brine, 30° | 6.8 | 3.5 | 3.3 |
| | 2 | | | 3.5 | 3.3 |
| | G-1 | Treated brine, | 5.8 | 3.6 | 3.4 |
| | 2 | 30°, pH 6 with $CH_3COOH$ | | 3.5 | 3.3 |
| | H-1 | New brine, 45° | 5.6 | 3.6 | 3.3 |
| | 2 | | | 3.5 | 3.3 |
| | J-1 | Treated brine, 45° | 5.7 | 3.6 | 3.4 |
| | 2 | pH 6 with $CH_3COOH$ | | 3.5 | 3.4 |
| | K-1 | Treated brine, 45°, | 10.9 | 3.7 | 3.4 |
| | 2 | pH 11 | | 3.7 | 3.4 |
| Susp. Solids, mg/l | F-1 | | 105 | 7930 | 860 |
| | 2 | | | 5630 | 1310 |
| | G-1 | | 84 | 8720 | 900 |
| | 2 | | | 4650 | 630 |
| | H-1 | | 129 | 2230 | 2450 |
| | 2 | | | 3490 | 730 |
| | J-1 | | 119 | 14,160 | 1080 |
| | 2 | | | 13,740 | 1470 |
| | K-1 | | 119 | 21,870 | 790 |
| | 2 | | | 5,020 | 1450 |
| Sugar, gr/100 ml | F-1 | | - | 0.60 | 0.05 |
| | 2 | | - | 0.48 | 0.02 |
| | G-1 | | - | 0.25 | 0.01 |
| | 2 | | - | 0.50 | 0.04 |
| | H-1 | | - | 0.50 | 0.03 |
| | 2 | | - | 0.62 | 0.08 |
| | J-1 | | - | 0.52 | 0.02 |
| | 2 | | - | 0.62 | 0.03 |
| | K-1 | | - | 0.62 | 0.03 |
| | 2 | | - | 0.74 | 0.03 |
| COD, g/l | F-1 | | 0.18 | 17.5 | 17.0 |
| | 2 | | | 17.3 | 16.5 |
| | G-1 | | 3.90 | 20.9 | 18.0 |
| | 2 | | | 18.7 | 18.4 |
| | H-1 | | 0.19 | 20.5 | 17.7 |
| | 2 | | | 22.4 | 14.1 |
| | J-1 | | 5.80 | 24.6 | 16.2 |
| | 2 | | | 23.6 | 18.2 |
| | K-1 | | 4.90 | 23.3 | 18.1 |
| | 2 | | | 23.9 | 17.7 |

TABLE 43 (continued)

| Parameter | Treatment | Elapsed Time 0 days | 6 days | 22 days |
|---|---|---|---|---|
| Kjeld-N, mg/l | F-1 | 10 | 700 | - |
| | 2 | | 825 | - |
| | G-1 | 125 | 1000 | - |
| | 2 | | 825 | - |
| | H-1 | 8 | 875 | - |
| | 2 | | 1050 | - |
| | J-1 | 195 | 1100 | - |
| | 2 | | 1150 | - |
| | K-1 | 190 | 1075 | - |
| | 2 | | 1075 | - |
| $NH_4$-N, mg/l | F-1 | 2 | 195 | - |
| | 2 | | 185 | - |
| | G-1 | 90 | 275 | - |
| | 2 | | 235 | - |
| | H-1 | 2 | 225 | - |
| | 2 | | 230 | - |
| | J-1 | 140 | 315 | - |
| | 2 | | 280 | - |
| | K-1 | 130 | 265 | - |
| | 2 | | 260 | |

## Discussion and Conclusions

A major factor to consider in reuse of 36-hr and spent brines is their softening enzyme (pectinase) content. Pectinase activity can be eliminated in these brines by coagulation-precipitation at high pH. Treatment of brines by this method also removes phosphate and drastically reduces bacterial populations. However, it does not remove the majority of the organic component as measured by TOC or COD analysis. Brinestock brined in high pH treated brine (one reuse cycle) compares favorably with that brined in new brine. Pickles packed as sweet or dill after brining in reused brine are not significantly different in quality from those brined in new brines.

In these studies brine was reused only once. There is some question as to buildup of metals, organic compounds, or other materials during repeated reuse. In the long run, feasibility of treating brine for reuse will be dependent on whether removal of pectinase activity alone will suffice, or whether removal of all organic compounds and/or metals will be necessary. In the latter instance, the coagulation-precipitation method described here would be inadequate.

Treatment and reuse of spent brines on a large-scale basis offers potential for greatly reducing the salt load on the wastewater treatment system and on the receiving stream, as well as for greatly reducing salt costs. Assume a plant

**using 6,700 tons of salt per year (10,000 tons at present, minus 3,300 tons saved by better housekeeping); assume 90% of the 6,000 tons remaining in the spent brines can be recovered by coagulation-precipitation or ultra-filtration. Reuse of this 5,400 tons would eliminate that load on the receiving stream and in addition, offer a potential savings in salt costs, depending on the cost of treatment.**

# BIOLOGICAL TREATMENT OF WASTEWATERS FROM CUCUMBER PICKLING

## Introduction

The only rational basis for undertaking wastewater treatment is correction of deficiencies in quality which could cause harmful environmental impact. Wastewaters from the pickle industry contain several types of constituents which potentially could cause such difficulties, including suspended matter, biodegradable organics, and chlorides. Technology is available for removal of any or all of them to any extent desired, subject only to financial limitations.

Biological treatment, which includes the types of systems most commonly installed today, is concerned principally with destruction and removal of biodegradable organics and, to a lesser degree, suspended matter. It must be recognized that biological treatment has no impact on chloride contents of wastewaters. Removal of chlorides would require application of entirely different technology.

## Goals of Biological Treatment

Biodegradable organic chemicals are those which can be utilized by bacteria and other microorganisms as sources of energy and elements required by them to form additional cell material (growth). Biochemical utilization of the organics leads to their breakdown into simpler chemicals and, perhaps, ultimately to inorganic ash and gases.

Although biodegradable organics in wastewater discharges may be objectionable for many reasons, the concern most often encountered is based on their impact on dissolved oxygen resources in receiving streams. This can be attributed to the fact that processes involved in biochemical transformation of carbon in organic compounds include utilization of oxygen and production of carbon dioxide. The oxygen required is obtained by the organisms from dissolved oxygen in the receiving water, thereby imposing a "biochemical oxygen demand" (BOD) on the limited supply of that gas in the stream. The total amount of BOD exerted depends upon the amount of organic chemical discharged and the extent to which it is biodegradable. The rate at which exertion occurs is influenced by many other variables, as well, including the numbers and types of organisms present and several environmental factors, including temperature and pH.

If dissolved oxygen in the stream is used more rapidly than it can be replaced from the atmosphere, and through photosynthesis by algae, its concentration will decrease. As more organics are added to a stream, dissolved oxygen concentration is reduced to progressively lower levels until, eventually, adverse effects are observed on survival of various types of fish and fish food organisms. Addition of sufficient organics to exhaust completely the supply of this essential element can render the water unsuitable for supporting any fish life. Further, under those circumstances, other types of biochemical reactions may lead to production of foul odors in the vicinity of the stream.

For many years, depletion of dissolved oxygen has been the stream pollution problem receiving greatest attention in the U.S.A. One should recognize that this concern about dissolved oxygen levels in streams and lakes is not based on concern about human health because it never has been demonstrated that any relationship exists between dissolved oxygen content of the water and health of the population consuming that water. Accordingly, stream pollution problems relating to dissolved oxygen, and treatment processes directed towards removal of constituents causing BOD, are based primarily on maintenance of water quality adequate for support of aquatic life, protection of recreation uses, and prevention of local nuisances.

One way in which these problems can be minimized or eliminated is through removing biodegradable organics from the wastewater prior to discharge. The origin and basic rationale for biological treatment is based on the concept of providing facilities in which environmental conditions are maintained to encourage completion of the biochemical reactions before discharge of the wastewater. Thus, biological wastewater treatment processes only cause those reactions to occur in the treatment plant before discharge which otherwise would occur subsequently in the receiving stream anyway. The difference, of course, is that by causing the reactions to occur before discharge the impact on dissolved oxygen in the stream is minimized.

This goal generally is accomplished simply by accelerating reactions in the treatment facilities to reduce necessary holding time and required land areas. That is done through providing optimum environmental conditions and increasing the numbers of microorganisms coming in contact with the organics during treatment.

## Types of Biological Treatment Systems

Of all biological treatment systems, the oxidation pond is the one which most closely approximates what happens in receiving streams and this unit has a deceiving appearance of simplicity. The physical facility consists simply of a basin providing a holding time of weeks or months, depending upon character of the waste, during which bacteria and other organisms can degrade organics in the wastewater. The reactions are the same as those which would occur over a period of many days in the receiving stream if the wastewater were discharged without treatment. Oxygen required to satisfy needs of the process and to avoid nuisances is furnished principally through photosynthesis by algae growing in the pond. Algae are microscopic green plants having capability for utilizing carbon dioxide and producing oxygen in the presence of sunlight. Because energy required for the process is derived from sunlight, the rate of oxygen supply is controlled by the amount of sunlight intercepted and, therefore, pond area becomes the controlling design parameter. The high concentrations of biodegradable organics, and the corresponding oxygen demand exerted, in wastewaters from even a moderate size pickle processing plant would require many acres of oxidation ponds, even under the best of conditions.

Frequently, it is more economical to provide biological treatment through using aerated lagoons. Again, the basic reactions which occur in these units are the same as those in oxidation ponds or receiving streams. However, required land areas are smaller because oxygen is supplied through man-made aeration systems which enhance transfer from the air to pond contents. The aeration can be accomplished by introducing compressed air into the basin, resulting in transfer of oxygen from bubbles into the liquid, or by surface aerators which cause violent agitation and enhance transfer of oxygen through the pond surface or into liquid droplets. Adoption of this type of system *removes* the constraint of having to provide large surface area to intercept adequate sunlight and leaves as primary design parameter the retention time of the wastewater in the pond. In practice, the time provided depends upon strength of the waste, its characteristics, pH, temperature and other eqvironmental factors, as well as required quality of effluent from the system. Frequently, aerated lagoons are constructed by industries with retention times of 5-100 days. The high concentrations of organics in wastewaters from pickle processing have led to construction of facilities of 15-60 days.

The types of organisms which develop during biological treatment of most wastewaters have specific gravity slightly in excess of water and tend to agglomerate into particles large enough to settle at reasonable rates. Effluent from an aerated lagoon, for example, can be passed through a settling tank of approximately two hours retention, causing separation of most of the organisms from the liquid under the influence of gravity. Liquid from the bottom of this unit contains substantially higher concentrations of microorganisms and can be returned to the aeration basin to increase their population in that unit.

The rate of attack on organic constituents of wastewaters entering the aeration basin increases in proportion to population of viable organisms, resulting in increased treatment capacity in systems based on aeration, final settling, and return of the settled sludge. This approach is termed the "activated sludge" process. Although there are many different versions, all of them accomplish the same purpose - they accelerate the rate of biological destruction of organics by increasing the supply of organisms in contact with the wastewater. This allows more extensive treatment in a given facility, or permits construction of a substantially smaller plant to accomplish a specified degree of treatment of a given wastewater. Still, the biochemical reactions which occur in this type of system are basically the same as those which would occur in receiving streams, oxidation ponds, or aerated lagoons.

## Applications in Pickle Industry

Although several other biological treatment processes are available, and there are many modifications of ones already outlined, the types of facilities most commonly provided for treatment of wastewaters from pickle processing are aerated lagoons or activated sludge systems. Where adequate land is available at reasonable cost, the aerated lagoon usually is simpler and more economical. Where space is at a premium, activated sludge represents a more reasonable approach. Several aspects of these processes, combined with certain characteristics of wastewaters from the pickle industry, deserve at least brief attention.

It was pointed out earlier that biological treatment does not have significant impact on chloride content. On the other hand, it is possible that chlorides can have adverse effects on biological treatment because at sufficiently high concentration, growth of organisms may be inhibited. However, this effect usually is observed only at very high concentrations of chlorides and it appears at least doubtful that their inhibiting effects would be important at the levels commonly encountered in total wastewater flow from pickle processing.

A different adverse effect of chlorides on the activated sludge process can result from increased specific gravity of wastewater with rise in chloride concentration. That sometimes could interfere with settling of organisms, which typically have specific gravity very close to that of water. Of course, any thing which impedes separation of organisms in the final settling tank can preclude adequate concentration for attainment of levels in the aeration tank which produce acceptable treatment rates. The exact magnitude of chloride effects in treating pickle processing wastewaters in practice is not known currently.

A further consideration is that potentially harmful effects of chlorides may be magnified considerably in situations where they swing rapidly through wide ranges of concentration. These changes can be more harmful to aquatic life than sustained operation at either low or high concentration. This question deserves serious consideration and should be explored carefully, especially in any treatment system in which it is planned to use short retention activated sludge, where chloride concentrations may vary quickly.

A factor which sometimes is given too little consideration in planning and design of treatment facilities is production, handling and disposal of sludge. In any biological treatment system, the biochemical reactions result in partial destruction of biodegradable organics and utilization of some of the remaining wastewater constituents to produce new biological cells (growth). The proportions destroyed and converted into cells vary considerably depending on character of the chemical, environmental conditions, and period of retention in the system. Generally, aerated lagoon and activated sludge systems similar to those employed for treating wastewaters from the pickle industry produce net microbiological growth in the range of 0.1-0.5 pounds of suspended solids for each pound of BOD removed from the wastewater. Failure to remove these solids from the system in amounts corresponding to their net production must result in accumulation in the treatment plant. There, they either settle and reduce effective volume of the aeration tank or escape from the plant, which often is unacceptable because of limitations on effluent suspended solids and because those suspended solids themselves exert a BOD.

The present trend in requirements for effluent quality suggests that very soon it will be necessary for virtually all plants to provide facilities for sludge handling. Some alternatives which can be considered include providing very large sludge holding lagoons, land disposal, or sludge dewatering on drying beds, vacuum filters or sludge centrifuges followed by disposal in sanitary landfills, application to land or incineration. Usually, it is impossible for a biological treatment facility to meet standards imposed upon it by EPA and State agencies without careful management of suspended solids. Sludge handling problems undoubtedly will cause serious difficulties and major expense to most pickle processors and, often, may cost more to solve than construction of the biological wastewater treatment plant.

Operating problems occur sometimes *in* treating pickle processing wastewaters because of pH variations. Organic acids in the wastewater and production of even more organic acids during biological treatment can cause sharp decrease in pH in the aeration tank, even though the wastewater being treated is initially about neutral in pH. Successful biological treatment requires maintenance of reasonably uniform pH, usually in the range of 6-8. Rapid variations and departures substantially outside of that range usually are harmful to the process and result in lower treatment efficiency.

Activated sludge and aerated lagoon systems are basically aerobic processes, requiring presence of excess dissolved oxygen to attain optimum treatment and avoid odorous conditions. Inadequate oxygen supply can permit dissolved oxygen concentration in the aeration tank to drop below 1 mg/l and, perhaps, exert significant adverse impact on treatment. Wastewaters from the pickle industry may suffer unusually serious impact from inadequate aeration because resulting increases in concentrations of organic acids also can cause drop in pH, interfering with biological treatment because of low pH and low dissolved oxygen. This makes it especially important in treating wastewaters from the pickle industry to insure that dissolved oxygen in the aeration basin always is maintained at least above 1 mg/l. This requires provision of more conservative air supply, including standby equipment to cover failtures, and emergency neutralization equipment for addition of alkali to the aeration tank to prevent pH drop.

Biological treatment has been applied to pickle and olive wastes with good results if critical operating parameters are controlled. Barnes and Weinburger (1958) reported the use of trickling filters, activated sludge, and oxidation ponds for pickle wastes, but no details were given. Hazeltine (1952) conducted pilot studies on trickling filtration of sauerkraut and pickle wastes and concluded that with proper pH control and loading 85% or more reduction of BOD could be achieved. He found that chloride concentrations of up to 5000-6000 mg/l had little effect on treatment efficiency. Burnett (1974) reviewed effect of salinity variations on the activated sludge system; high salinity could be tolerated if sharp variations were avoided.

Ail North Carolina plants currently use aerated lagoons for waste treatment. In some cases plant growth has outstripped treatment facilities, as is exemplified by Plant A. Plant A has two aerated lagoons, each with a capacity of close to '2 MGD. These ponds were designed tc accommodate 100,000 gpd of wastewater, giving a total detention time of 40 days. However, the average hydraulic load consistently exceeds the design load by a factor of 2 or more (Table 30). A similar situation exists at Plant B. Personal observations and observations by plant personnel indicate that the dissolved oxygen level is frequently below that required for aerobic degradation of wastes. The low DO, coupled with shortened detention time, low pH, and high chloride levels, has resulted in marginal biological treatment efficiency.

Discharge of pickle wastes to municipal biological treatment systems has resulted in problems in a number of cases. Kimball (1960) reported the effect on a municipal system in Crosswell, Michigan when increased demand *for* sweet pickles and relish caused a tripling of the BOD load from a local pickle plant. Not only did the efficiency of the Imhoff tank - trickling filter system drop from 85 to 56%, but odor and corrosion problems developed. In a North Carolina town some years ago the municipal Imhoff tank system had to be abandoned when wastes from the local pickle plant rusted out the system.

## Effects of Treated Effluent on Receiving Streams

As pointed out previously, biological treatment does not affect chloride concentration of pickle plant wastewaters. Discharge of high concentrations of salt can cause numerous undesirable effects of receiving streams. Such effects have been reviewed and summarized by Field et al. (1973) and McKee and Wolfe (1963) and include the following:

(1) density stratification in receiving streams

(2) release of mercury from sediments due to exchange of mercury with sodium and calcium
(3) groundwater pollution
(4) increased corrosion rates
(5) toxicity to freshwater fish
(6) interference with use of water for stock and wildlife watering if salt exceeds 1500 mg/l
(7) interference with use of water for irrigation

Salt-tolerance varies with different crops. Crop species especially sensitive to salt include green and field beans, celery, radish, citrus fruits, pear, apple, plum, peach, and avocado (Field et al., 1973) and tobacco (personal communication, P. Benton, N. C. Water and Air Resources, Industrial Wastes Section). The overall amount of acreage irrigated in North Carolina is -105,000 acres; in Michigan, 139,000; and in Delaware, 15,000 (Skogerboe , 1971) .

McKee and Wolfe (1963) cited the following recommended chloride limits: domestic water supply, 250 mg/l; industrial water, 50 mg/l; irrigation, 100 mg/l; stock and wildlife, 1500 mg/l.

<u>Conclusions</u>

Biological treatment is designed to remove biodegradable organics from wastewater prior to discharge. It has no impact on chloride content. However, high chloride levels may interfere with biological treatment, especially if there are sharp variations in concentration.

The organic component of pickling wastewater is readily treated biologically if sufficient detention time and sufficient dissolved oxygen are available(see Appendix A). Since much of the acidity is due to organic acids, aerobic biological treatment will also reduce or eliminate the need for pH adjustment with alkali.

There are numerous adverse effects of chlorides on receiving streams. The level of chloride considered "adverse" is highly dependent on the intended use of the stream.

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## GLOSSARY

Abbreviations, Units

| | | |
|---|---|---|
| hr | - | hour |
| gal | - | gallon |
| gpd | - | gallons per day |
| l | - | liter |
| ml | - | milliliter |
| mg/l | - | milligrams per liter |
| mmhos | - | millimhos |
| MW | - | molecular weight |
| | - | micron (+ nannometer |

Abbreviations, Terms

| | | |
|---|---|---|
| BOD | - | biochemical oxygen demand |
| Cl | - | chloride |
| COD | - | chemical oxygen demand |
| DO | - | dissolved oxygen |
| Kjeld-N | - | total Kjeldahl nitrogen |
| $NH_4$-N | - | ammonia nitrogen |
| $NO_2$-N | - | nitrite nitrogen |
| $NO_3$-N | - | nitrate nitrogen |
| spec. cond. | - | specific conductivity |
| SS | - | suspended solids |
| TDS | - | total dissolved solids |
| TOC | - | total organic carbon |
| TP | - | total phosphorus |
| TS | - | total solids |

APPENDIX A

# INDUSTRIAL WASTEWATER SURVEY OF A CUCUMBER PICKLE PLANT

by

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A Report

from

Department of Environmental Sciences and Engineering
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The University of North Carolina at Chapel Hill

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# ABSTRACT

*Manufacture of pickles results in large quantities of wastewater that are not easily treated. The pickle plant studied in this project presently is under pressure* from *the State Board of Water and Air Resources to implement more adequate treatment of its wastewater discharges. The combination of present treatment facilities and operating procedures are judged to be inadequate to achieve proper treatment of the low pH, high organics and high salt content of effluents generated.*

*This investigation was undertaken to examine some areas of concern in production and treatment of the wastewater to provide a basis for* improving *procedures and facilities to reduce present treatment difficulties.*

*An inventory was conducted to determine the volume and character of wastewaters generated within the plant. Further, the contribution of wastes from each plant manufacturing area was studied to determine where changes would be most effective. Flow measurements and wastewater sampling and analyses* were *employed to yield desired information, summarized in the report.*

*Neutralization of plant wastewater with three common alkalis was studied to compare their relative effectiveness. Small quantities of effluent were titrated with aqueous ammonium hydroxide and sodium hydroxide and with calcium hydroxide. A comparison of the neutralizing capacity of these alkalis for this particular waste was obtained. Large quantities of alkali may be required to raise the pH of the lagoon before biological treatment can be effective. Continued smaller additions may be needed to maintain proper pH within the system. Sodium hydroxide appears to be the chemical of choice.*

*Pilot treatability studies were conducted at bench scale to evaluate biological treatability by aerated lagoons and effects of variations in pH and salinity on biological treatment of wastes from the Henderson plant. Treatment facilities at the plant were simulated in each laboratory pilot unit through use of a series of three aerated columns. Daily plant effluent additions and transfers were made. Three conditions were studied: 1) neutralization to pH 7.0; 2) neutralization to pH 7.0 along with increased salinity and 3) neutralization to pH 5.5. Results indicated extensive removals of organics and revealed only slight differences in treatment provided for the wastes of different pH. Most of the organics removal is accomplished in 15-30 days detention.*

*Finally, a respiration study was carried out to demonstrate the effect of shock loads on the treatability of plant wastes. By measurement of dissolved oxygen uptake by treatment organisms, it was possible to examine the effects of large differences in salt content and acidity on treatability. These were less than had been anticipated.*

## INTRODUCTION

The plant surveyed produces pickles from cucumbers and other vegetables and discharges wastes which are high in organic content (BOD), suspended solids, chlorides and organic acids, causing a low pH. They are treated in aerated lagoons before discharge into a small creek, a small tributary of a reservoir. The treatment facilities consists of 6.7 million gallon aerated lagoon, partitioned by baffles to provide continuous flow in series through four equally sized basins. A Hinde Air-Aqua system provides submerged aeration throughout the entire lagoon. The lagoon originally was designed with a detention time of sixty days for an effluent flow estimated at 100,000 gal/day.

Effluent from the lagoon has had an adverse effect on stream water quality in the receiving creek according to the North Carolina State Board Water and Air Resources, which has ordered the plant to correct the deleterious effect on the tributary. Specific areas of concern include BOD, suspended solids and chloride loadings, in addition to pH.

This preliminary study of the problem was undertaken as a special project by a class studying "Industrial Water Quality Management," a course in the Department of Environmental Sciences and Engineering, the University of North Carolina at Chapel Hill.

## EXISTING TREATMENT FACILITIES

All industrial wastewater flows from the plant, including those related directly to preparation of product, cooling waters, cleanup flows and storm runoff, are collected in a single sewerage system for treatment and disposal. The combined flow is screened for removal of some of the large suspended matter and currently is subjected to treatment in an aerated lagoon before discharge.

The screening operation is manual and has been observed during plant visits to be sufficiently clogged to permit overflow of unscreened wastewater into the aerated lagoon. Flow passing through the screen is discharged into the lagoon near one end of the first "bay."

The aerated lagoon is approximately 270 ft wide by 330 ft long, with 10 ft water depth. It is divided into 4 bays by 3 longitudinal timber baffles, with openings at alternate ends which permit passage of flow through them in series. Condition of the facility suggests that some of the flow may short-circuit through leaks in the baffle walls, but that is not viewed as a serious problem in view of the long detention period.

Total volume of the aerated lagoon is about 6.7 million gallons, providing detention of 67 days at the design flow of 100,000 gal/day. Actual flows through the plant are substantially higher than the design value, however, especially during the fresh pack season and when there is runoff during rainfall. This results in actual detention periods substantially lower than the design value.

Air supply is provided by two 40 hp blowers, rated at 595 cfm each. The air diffusion system is based on use of perforated plastic pipe (Hinde Air-Aqua system). Because some of the tubes are submerged in bottom deposits and have clogged orifices, the air diffusion pattern throughout the basins is somewhat irregular and the rate of air application appears to be too low, at least by visual estimate.

Recently an additional facility was installed to permit metering of flow entering the aerated lagoon, neutralization with sodium hydroxide or ammonium hydroxide, and addition of nutrients. The Parshall flume, pH control equipment and nutrient addition facilities were not in operation during these visits. The low elevation at which the facilities were installed, apparently, will require lowering the water level in the aerated lagoon and reduce effective volume of that unit when operation of the new facility is initiated later.

A 1970 report of the North Carolina Department of Water and Air Resources indicated influent BOD values ranging from 700-5,000 mg/l, with effluent BOD of 3100 mg/l. pH of the influent waste was 3.6-4.2 and pH in various sections of the aerated lagoon varied from 3.4-4.1, leading to a recommendation that the waste be neutralized with sodium hydroxide or ammonium hydroxide. Analyses for nutrients indicated presence of about one-half the recommended levels of nitrogen and phosphorus and addition of both nutrients on a regularly scheduled basis was recommended. The report indicated that the treatment facilities were not performing as designed (14% BOD removal instead of 90%) because of low pH, nutrient deficiencies, high chloride content, and inaccurate selection of design BOD load.

## PURPOSE AND SCOPE

The class undertook a limited in-plant study of processes and practices, and investigated biological treatability of process wastes by aerated lagoon. The period of study was March-April, 1974. During this "off season" major plant activities are repair and maintenance of brine tanks, the firming process, processing and packing of sweet and sour pickles, and relish-making operations, all using pickles stored in brine (brine stock). The volume and nature of wastewaters produced and the range of activities are substantially lower than in the "green season."

Four operating processes within the plant were identified as major sources of wastewater. Grab samples were collected and analyzed to determine waste constituents and attempts were made to measure flows generated by each process. Plant practices were observed and suggestions offered for their modification to reduce waste materials reaching the lagoon.

The treatability studies focused on determination of whether wastes with these characterists can and should be treated biologically and, to a limited extent, under what conditions. Also, laboratory studies were conducted to determine which alkali would be most effective in neutralizing the low pH plant effluent. Shock effects of low pH and changes in chloride levels on biological activity of the organisms were examined through respiration rate studies. Of necessity, all of these studies were conducted within a limited time frame.

## IN-PLANT SURVEY

### Objective

The objective of this phase was identification of the many chemical and organic constituents of the wastewater and measurement of the volume of wastewater contributed to the lagoon by each of four plant operating areas: 1) the processing room where cucumbers are colored and finned, where sweet pickling is accomplished and where relish is chopped and prepared; 2) the manufacturing and packing area where pickles are sliced and where products are packed into jars and capped; 3) the pasteurizing area where the sealed jars are pasteurized, labeled and packed for shipment; and 4) the tankyard,

### Procedure

Since a limited study had been done previously by a company engineer, a decision was made to utilize the same sampling points so that data might be compared. A sketch of the drainage system is shown in Figure 1. The processing room sample point was a large, shallow, open manhole (Drain 15B) on the hill overlooking the lagoon. Three tankyard drains also emptied into this manhole but the wastes could be distinguished one from another due to three separate and easily sampled discharge pipes within the manhole.

Two sampling points were identified in the manufacturing area. The waste collection box at the end of the drain under Line 6 served as one sample point, collecting wastes from the capping lines and the pickles being packed on Line 6. The second sampling point was the waste collection box approximately 15 feet below the confluence of the drains serving Lines 3 and 5 and the sorting and cutting area. In the pasteurization area, samples were collected from the drain two feet upstream from its discharge to the waste collection box.

Flow measurements were made with a four-gallon bucket and stop watch. This method was not satisfactory for in-plant sampling due to the condition of the drains which did not permit a free flow into the bucket. The large volumes of water discharged from the pasteurizing room at Drain 15B also made measurement difficult.

One night was spent observing the cleanup crew.

A few simple experiments were also carried out on a pilot size screening device (hydrasieve) to determine its applicability for screening solids from the lagoon influent.

All chemical tests on the samples collected were performed in accordance with the procedures outlined in Standard Methods' for the Examination of Water and Wastewater. The laboratory analyses were conducted by the UNC Wastewater Research Center.

## Results

From a survey of the wastewater flows it was found that the drainage system from the pasteurizing area also collected wastes from the concentrated brine and pickling liquor preparation area. The processing room drains directly to the lagoon through a pipeline which also collects storm runoff from the railroad yard and salt storage area. The manufacturing-packing area and the pasteurizing area drain to a sewer running in front of the building, which also collect wastes from the boilers and tankyard before emptying into the lagoon.

Silt observed in all tankyard drains and during periods of heavy rainfall is carried to the lagoon. Several tankyard drains were completely clogged and had apparently been so for some time since storm runoff and tank drainage had worn deep rivulets in the hillside around and alongside the drains. The steep hillsides around the lagoon are essentially barren permitting sediment to be carried to the lagoon. Siltation in the lagoon contributes to the clogging of the air bubbling system and to the need for dredging.

Screens were used on several of the inside drains in an attempt to prevent large pickles and pieces of pickle from reaching the lagoon. These screens were generally in poor condition and often did not fit properly. The basket screen at the end of Lines 3 and 5 functions only during periods of high flow. During periods of low flow the deteriorated condition of the drain lip allows wastes to run under the basket and directly to the sewer. The screens were generally observed to need cleaning. Several times employees were observed removing the screens and flushing screened materials into the sewers.

The influent screen at the lagoon was clogged with screened materials on every visit. On several occasions the effluent poured over the clogged screen into the lagoon carrying large pieces of material with it. Solids removed from the screen were piled on the ground to one side where rainfall overflow washed them directly into the lagoon.

From observing the night shift cleanup crew, it was noted that the poor condition of the flooring in the packing area hindered attempts to sweep the floor clean and necessitated the use of additional hosing to remove food particles trapped between the bricks in the floor. These food particles were hosed to the drains and subsequently into the sewers. Attempts to encourage plant personnel to measure the volumes of water used in evening cleanup by reading the water meters were unsuccessful. Accordingly, no data was collected on this activity.

The analytical data and flow measurements are summarized in Tables l-5. All of the wastes were acidic, with pH generally less than 4.0. The most acidic wastes were generated in the processing area and Line 6 of the manufacturing-packing area.

Examination of the combined pasteurizing, manufacturing-packing and boiler room effluents collected at a manhole outside the building show lower BOD, total solids, organic carbon and acidity presumably due to dilution. Chlorides and pH, however, remained substantially unchanged, for which there currently is no explanation.

Extremely simple preliminary tests on plant wastes indicate a strong potential for the reduction of organic loading through the use of a Hydrasieve as seen from the reduction in DOD and solids given in Table 6.

Discussion

Experience during this limited study indicated that the wastes do not lend themselves to grab-sampling or unsophisticated flow measurements. There was high variability in both volume and nature of the wastes during this two-month period of the off-season. Reliance on averages and extrapolation of data collected during the off-season to the "green season" is both unrealistic and unreliable. A well-planned, organized study over an entire year of the manufacturing process and of the wastes it generates is needed to provide a comprehensive and realistic analysis of the volume and nature of the wastewater involved and to determine those areas of the plant where in-plant process changes and water conservation will substantially reduce waste effluent. This study must be backed up by competent and full laboratory analyses of wastes so that the best treatment methods may be determined. Short cut solutions will only result in capital expenditures which offer little or no improvement. The age and operation of this processing plant together with variable nature of its wastes necessitates the services of a consulting engineer to develop a satisfactory solution.

The volume of wastes generated in those processes having the greatest brine concentration, the highest oxygen demand and the lowest pH determine

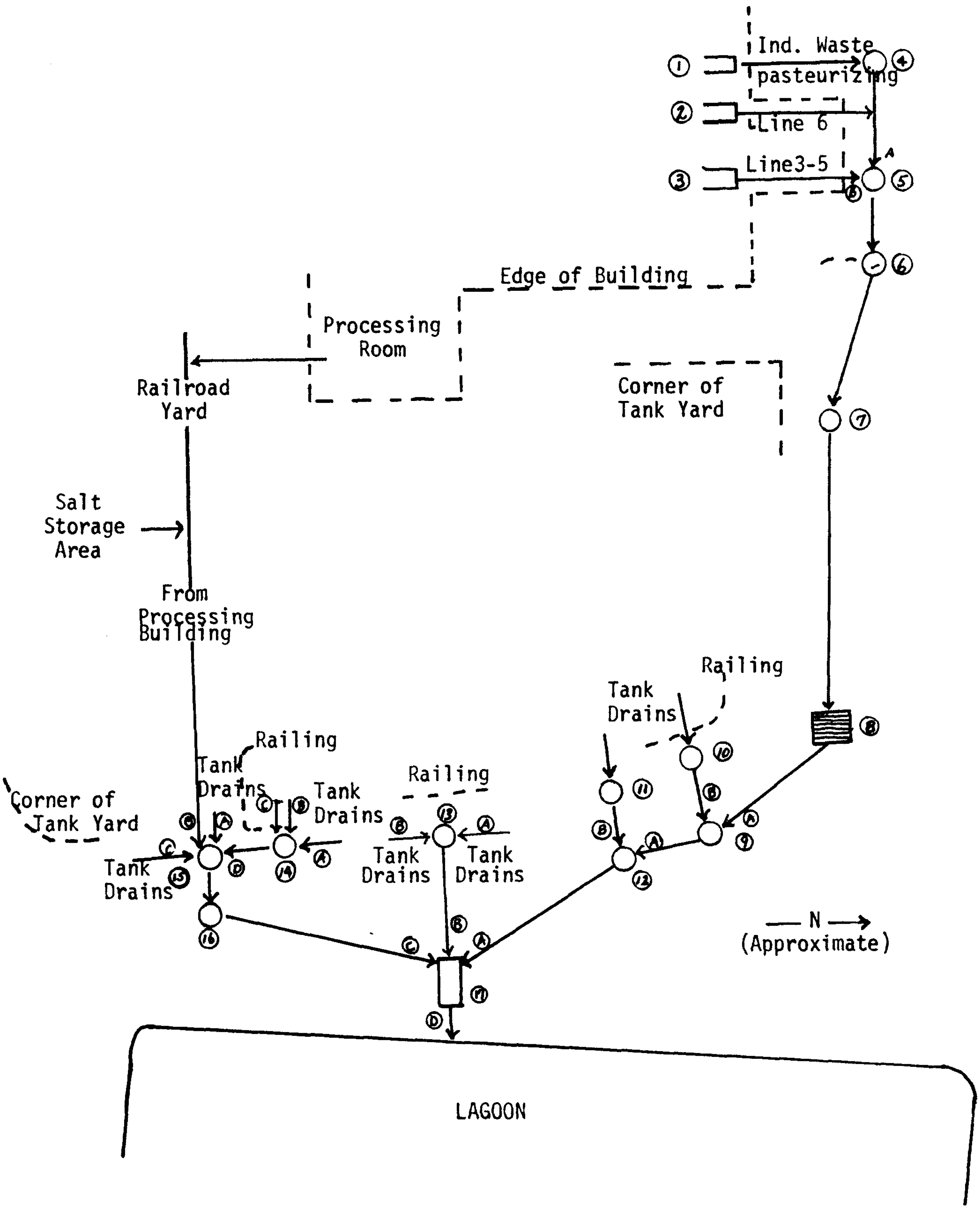



FIGURE 1. SKETCH OF SEWER SYSTEM AT PLANT

TABLE 1. PROCESSING ROOM GRAB SAMPLES COLLECTED AT DRAIN 15B

| | March 27, 1974* | | | | April 3, 1974 | | | | April 11, 1974 | |
|---|---|---|---|---|---|---|---|---|---|---|
| Date Time | 1540-1605 | 1540-1605 Imhoff Cone Super-natant | 1540-1605 Imhoff Cone Super-natant | 1735 | 1445-1500 | 1607* | 1645-1700* | 1705* a | 939 a | 951 b |
| Analysis | Composite | | | | Composite | | Composite | | | |
| Organic Carbon | 11,800 | 16,200 | 16,200 | 10,400 | 1,050 | 7,800 | 1,400 | 1,150 | 850 | 1,100 |
| BOD (mg/l) | 21,600 | >24,000 | >24,000 | 21,900 | 1,050 | >9,480 | 2,400 | 2,040 | 1,800 | >2,490 |
| Total Solids (mg/l) | 33,665 | 49,303 | 49,565 | 26,187 | 30,805 | | | | 15,077 | 70,334 |
| Suspended Solids (mg/l) | 283 | 89 | 120 | 99 | 511 | 1,025 | 111 | 175 | 28 | |
| Settleable Solids (mg/l) | | 25.5 | 20 | | 142.5 | | | | 1.5 | |
| pH | 3.7 | 3.4 | 3.4 | 3.8 | 3.7 | 3.6 | 3.8 | 3.8 | 3.7 | 3. |
| Acidity | 1,149 | 3,000 | 2,811 | 900 | 429 | 969 | 566 | 471 | 506 | 549 |
| Specific Conductance (mmhos) | 18 | 15 | 15 | 8.4 | .41 | 42 | 34 | 30 | 18 | 52 |
| Chlorides | 7,400 | 6,500 | 6,500 | 3,300 | 16,810 | 18,542 | 14,518 | 11,869 | 8,500 | 28,300 |
| $PO_4$ as P (mg/l) | 5.5 | 4.7 | 6.5 | 2.2 | 9.0 | 10.8 | 3.3 | 2.6 | 0.9 | 18. |
| $NO_2$ and $NO_3$ as N (mg/l) | | | | | 1.0 | | | .7 | 1.0 | |
| $NH_3$ as N (mg/l) | | | | | 21.5 | | 12.5 | 12.5 | 1.0 | |
| Kjeldahl N as N (mg/l) | | | | | 82.5 | >50 | 62 | 50 | 24.5 | |

*Relish operation shut down

[a]Drain off the corner of the building near railroad track

[b]Waste well in the drainline between the waste well in the railroad yard and Drain 15 B

TABLE 2. PROCESSING ROOM DATA (DRAIN 15B)

| DATE | TIME | FLOW (GPM) | AVERAGE FLOW (GPM) | COMMENTS |
|---|---|---|---|---|
| March 27, 1974 | 1540 | 16.67 | | |
| | 1545 | 25.00 | | No relish operation |
| | 1555 | 32.69 | 24.84 | |
| | 1605 | 25.00 | | |
| | 1715 | 50.00 | | |
| | 1720 | 16.67 | 22.05 | |
| | 1725 | 11.54 | | |
| | 1730 | 10.00 | | |
| April 3, 1974 | 1445 | 160.00 | | |
| | 1447 | 160.00 | 162.86 | |
| | 1450 | 171.43 | | |
| | 1455 | 160.00 | | |
| | 1500 | 240.00 | | |
| | 1602 | 28.24 | | |
| | 1605 | 13.52 | 23.06 | |
| | 1611 | 27.43 | | Drain above 15 B |
| | 1649 | 160.00 | | |
| | 1650 | 171.43 | 163.81 | |
| | 1651 | 160.00 | | |
| April 11, 1974 | 935 | 40.00 | | |
| | | 46.10 | | |
| | | 46.10 | 44.76 | |
| | 939 | 43.6 | | |
| | | 48.0 | | |
| | 951 | 48.0 | | Well in drain between |
| | | 46.1 | | railyard and 15 B |
| | | 46.1 | | |
| | 955 | 43.6 | | |
| | | 40.0 | | |
| | | 38.7 | 39.9 | |
| | 1000 | 38.7 | | |
| | 1001 | 38.7 | | |

TABLE 3. CHARACTERISTICS OF WASTEWATER FLOWS FROM MANUFACTURING-PACKING AREA AND FROM PASTEURIZING ROOM

| | Manufacturing-Packing Area | | | | | | Pasteurizing Room | | |
|---|---|---|---|---|---|---|---|---|---|
| Date | April 3, 1974 | | | April 11, 1974 | | | April 3, 1974 | | April 11, 1974 |
| Analysis / Time | *1535 | 1547 | 1551(a) | 909 | 915(b) | 930(a) | 1620(c) | 1630(a) | 850(c) |
| | Line 3 and 5 | Line 6 | | *Lines 3 and 5 | | Line 6 | | | |
| Organic Carbon | 2,320 | 3,440 | 880 | 980 | 2,600 | 26,100 | 870 | 990 | 276 |
| BOD (mg/l) | >2,340 | >4,740 | 1,290 | >1,800 | >4,980 | 24,900 | 1,380 | 1,530 | >498 |
| Total Solids(mg/l) | 13,706 | 11,519 | 4,387 | 412 | 66,544 | 62,329 | - | - | 883 |
| Suspended Solids (mg/l) | 70 | 53 | 300 | - | - | - | 737 | 6 | - |
| Settleable Solids (mg/l) | 1.5 | | | 1.0 | 26.0 | | - | - | - |
| pH | 3.5 | 4.2 | 5.1 | 3.7 | 4.0 | 3.2 | 4.9 | 4.8 | 4.7 |
| Acidity | 831 | 291 | 86 | 154 | 386 | 2,108 | 146 | 86 | 60 |
| Specific Conductance (mmhos) | 13 | 5.2 | 4.1 | 2.9 | 49 | 5.1 | 2.10 | 746 μmmhos | 89 |
| Chlorides | 4,839 | 1,783 | 1,274 | 1,200 | 29,700 | 2,500 | 635 | 188 | 312 |
| $PO_4$ as P (mg/l) | 1.9 | 3.0 | 5.7 | 0.5 | 0.9 | 4.2 | 1.3 | 1.0 | .5 |
| $NO_2$ and $NO_3$ as N (mg/l) | | - | 1.1 | 0.9 | - | - | 0.7 | 0.8 | 0.7 |
| $NH_3$ as N (mg/l) | 6.0 | 3.5 | 4.0 | 1.0 | | | 8.5 | 5.0 | 1.0 |
| Kjeldahl N as N (mg/l) | >50.0 | >50.0 | >50.0 | 15.5 | | | >50.0 | 24.5 | |

*Composite drain serving lines 3 and 5 just prior to waste well
(a) Collected from waste well serving line 6 and the capping machines
(b) Hot pepper pickling liquid dumped into drain from transport vat
(c) Floor drain just prior to waste well

TABLE 4. CHARACTERISTICS OF WASTEWATER FLOW FROM DRAINS

| | Tankyard Drains | | Manhole Immediately Outside Boiler Room | |
|---|---|---|---|---|
| Date | April 11, 1974 | | April 11, 1974 | |
| Time | 1002(a) | 1005(b) | 1020(c) | 1030 |
| Organic Carbon | 1,500 | 1,500 | 1,130 | 930 |
| BOD (mg/l) | 2,490 | 2,490 | 1,350 | 1,770 |
| Total Solids (mg/l) | 49,150 | 71,430 | 3,711 | 3,496 |
| Suspended Solids (mg/l) | - | - | - | - |
| pH | 4.0 | 3.3 | 3.7 | 3.9 |
| Acidity | 300 | 883 | 300 | 197 |
| Specific Conductance (mmhos) | 52 | 74 | 2.8 | 2.6 |
| Chlorides | 28,700 | 38,900 | 1,100 | 1,100 |
| $PO_4$ as P (mg/l) | 7.4 | 38.0 | 0.9 | 0.5 |
| $NO_2$ and $NO_3$ as N (mg/l) | | | 1.1 | 1.0 |
| $NH_3$ as N (mg/l) | | | 2.0 | 2.0 |
| Kjeldahl N as N (mg/l) | | | 18.0 | 13.5 |

(a) Drain from that portion of tankyard lying to left as one stands facing lagoon (under Drain 15 B)

(b) Drain from that portion of tankyard lying to the right as one stands facing the lagoon (drain to right of 15 B)

(c) Manhole immediately outside boiler room

TABLE 5. FLOWS FROM MANUFACTURING ROOM - LINE 6

| Date | Time | Flow (GPM) | Average Flow (GPM) | Comments |
|---|---|---|---|---|
| 4/3/74 | 1545 | 7.27 | | |
| | 1547 | 6.15 | 6.33 | Line closing for the day |
| | 1549 | 5.58 | | |
| | 1550 | 20.00 | 20.00 | Machine washdown |
| 4/11/74 | 930 | Flow too small to measure; primarily from two capping units (condensed steam) | | |

TABLE 6. DATA FROM PRELIMINARY HYDRASIEVE TRIAL

Using Coarse Screen

| | |
|---|---|
| Influent Suspended Solids, mg/l | 113 |
| Effluent Suspended Solids, mg/l | 110 |
| Suspended Solids after settling, mg/l | 66 |
| Influent Settleable Solids, ml/l | 10 |
| Effluent Settleable Solids, ml/l | 7 |

Using Fine Screen

| | |
|---|---|
| Influent Suspended Solids, mg/l | 130 |
| Effluent Suspended Solids, mg/l | 55 |
| Suspended Solids after settling without screening, mg/l | 49 |

impact of the wastes on the lagoon. Therefore, it is imperative to acquire a close approximation of the contribution of each process to the total lagoon capacity over the different "manufacturing seasons" of the year. Monitoring of water lines to each individual process would provide information on how, where and when water is used and, teamed with good laboratory analyses of wastes generated, would permit determining the impact of each process on the lagoon. Times of potential shock loading in the lagoon could become apparent. Furthermore, this information would be useful in determining those plant areas where water conservation could make substantial contributions to waste reduction.

Organic suspended solids reaching the lagoon cause excessive oxygen demand and create accumulations of sludge which clog the air diffusion system and may necessitate occasional draining and dredging of the lagoon. High solids concentrations in the wastewater from the manufacturing-packing area apparently originated with draining of the coloring and firming vats, the wastewater from relish washings, the practice of dumping syrups left in vats after packing the products and poor cleaning practices in the manufacturing-packing area. Control of these wastes alone would greatly reduce the volume of organic materials reaching the lagoon.

From a standpoint of oxygen depletion, all of these wastes are important. The syru wastes are especially significant due to their excessively high oxygen demand.

The installation of a Hydrasieve on the lagoon influent would prevent many organic solids not trapped by in-plant screening from reaching the lagoon. Organic wastes too fine to be screened by plant floor drains and pickles and other vegetable products carried by tankyard drains to the lagoon could be effectively trapped thereby reducing the oxygen-demand on the lagoon.

## Recommendations

1. Retain a consulting engineer.
2. Meter the water flow to each process to obtain accurate data on the wastewater generated.
3. Reduce the solids reaching the lagoon in plant wastes.
   a) Initiate equipment and floor cleaning by dry sweep whenever possible. This may require closing manufacturing lines 15 minutes before the end of the shift and all factory line workers sweeping the machines with hand brushes and pans.
   b) Eliminate hosing of organic materials to the floor drains whenever possible. If hosing is required for final cleanup, utilize high-pressure, low flow hoses to reduce volume of wastewater generated, but only after dry sweep.
   c) Repair flooring in the sorting and packing area so that wastes may be swept up easily and not trapped between bricks requiring use of high-power hoses for flushing and cleaning floors.

d) Repair floor drains so that screens fit tightly.
e) Establish a program for routine maintenance of all floor drains, screens and waste collection boxes. Provide adequate disposal for screenings and discourage practice of flushing screened materials to sewer.
f) Evaluate the possibility of screening wastewater from the relish operation to remove fine pieces and their recovery.
g) Pickles on the floor or platforms should be swept up and placed in garbage barrels -- not flushed or swept into sewers or into the cracks around vats.
h) Exercise greater care in removing by netting the cut pickles from the alum process into the transport vats.
i) Establish routine maintenance for the influent screen at the lagoon and provide regular and adequate removal of screened wastes.

4. Install a Hydrasieve for the screening of lagoon influent.
5. Control tankyard erosion.
6. Establish clear communication between the decision-making offices, the laboratory and engineering and maintenance regarding policies and implementation of these recommendations.
7. Instruct plant personnel on the importance of all of these measures and why they must be accomplished.

## BIOLOGICAL TREATABILITY STUDY

In attempting to determine the treatability of wastes from this plant, many variables should be examined thoroughly. The fact that time available to this group for the study was rather limited required that some assumptions be made and that the group of factors studied be limited to a few of the most important ones.

It was assumed that before substantial improvement in the treatment system can be made, three conditions must be corrected. These include 1) removal, prior to discharge into the lagoon, of large organic solids in the plant effluent, 2) substantial increase in the volume of air supplied for aeration, and 3) possible addition of certain nutrients required by the microbial population of the treatment system but not available naturally in this wastewater in optimum quantities. These changes are considered prerequisite to proper treatment and were therefore incorporated into our study.

Once these conditions were eliminated or corrected, the two most important variables remaining and the ones which distinguish pickle wastes from practically all other food processing wastes are the low pH and the high chloride content. It was felt that knowledge of the effect of these factors on treatability would be most valuable in improving future treatment.

Therefore, three specific conditions were studied. They were (1) neutralization of plant effluent to pH 7.0, (2) neutralization to pH 7.0 plus slight increase in chloride content, (3) neutralization to pH 5.5. Comparison of 1 with 3 indicates the degree of neutralization necessary while comparison of 1 with 2 shows the effect of increased chloride content. Should large scale water conservation measures be practiced in the future without similar decreases in usage of salt, the chloride concentration of the lagoon could be expected to rise significantly above its present level.

The treatability study was designed to simulate treatment received in the lagoon. This was accomplished by daily batch additions of plant effluent, obtained from this plant and stored under refrigeration, to a series of aerated columns.

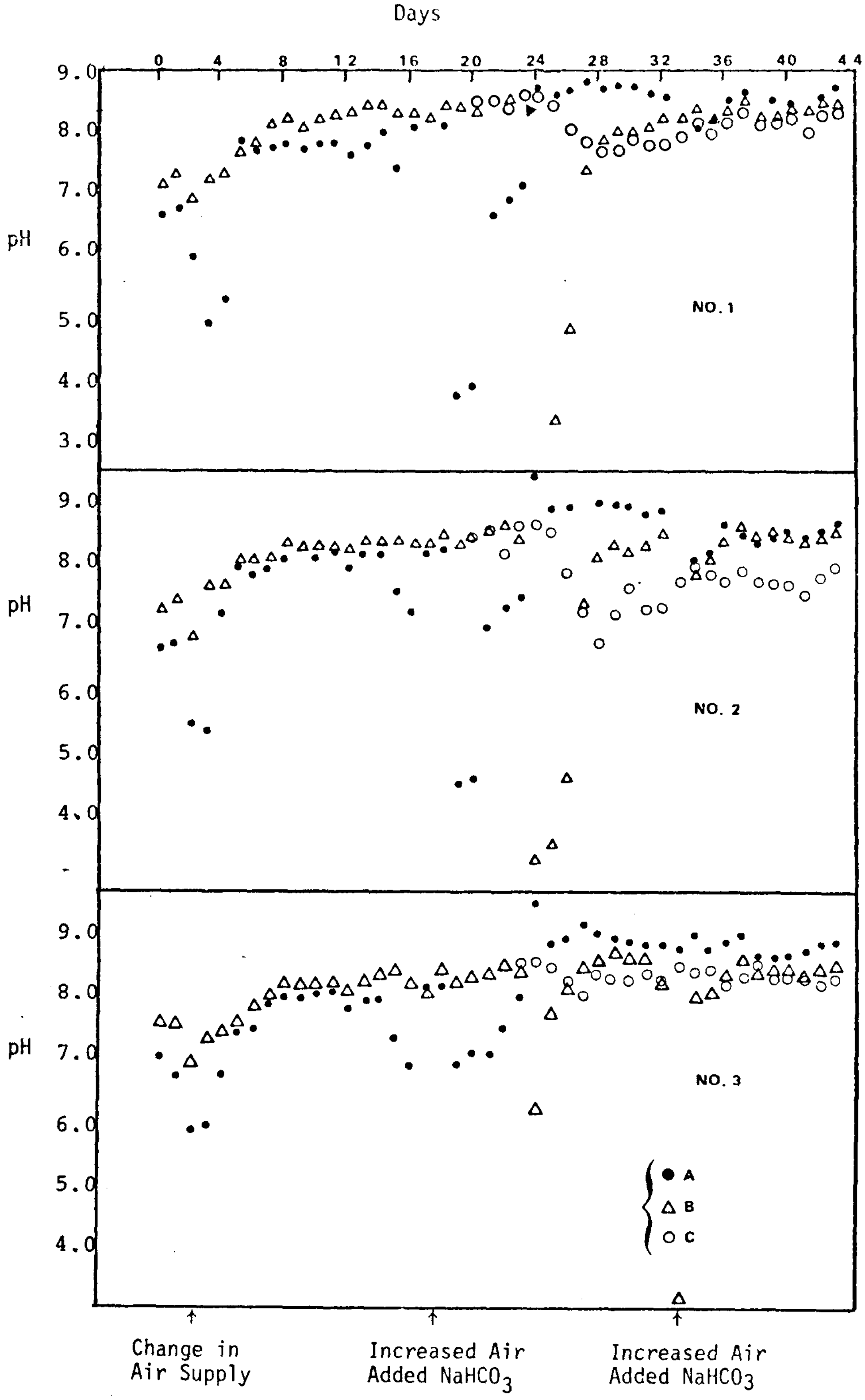
The cylinders simulated the first three stages of this plant's aerated lagoon. The nine columns ranged in height from 26-35 inches and in diameter from 3 3/4-4 l/4 inches. Several of these had conical bottoms while the remainder were flat bottomed. These minor variations in contour and dimensions should not have influenced the experiment. Each column had a tap on the side for removal of samples for transfer and analysis. No attempt was made to sinulate existing air supply conditions or to determine optimum air requirements. Instead we attempted only to maintain the air supply at a level such that there would be no concern for its adequacy. Air supply to individual columns was from a common manifold. Originally, diffusers were used for aeration. After several days these were replaced with large opening pipettes since the air flow was inadequate. Air supply was regulated by screw clamps.

The units were arranged in three numbered sets, each of which had three columns in series ("A," "B," and "C"). Each column contained 3 liters. The "A" (first unit of each set of three) columns were begun with a seed mixture of plant pond effluent, effluent from the trickling filter at the Mason Farm Sewage Treatment\Plant and Morgan Creek water. The other columns were empty. Each day, 200 ml (l/15 of the column volume) were removed from the "A" columns and added to the "B" columns until the "B" columns reached 3 liters. After that 200 ml were removed from "B" and added to "C" and from "A" to "B". Columns "A" were fed each day from a composite sample of lagoon influent collected 3 times a day at the plant. Several days' samples were mixed together for the feed. Since it was assumed that coarse screening would necessarily be provided, the sample was passed through coarse weave gauze which removed the large pieces of pickle but none of the smaller solids.

Losses due to evaporation were made up daily. Transfers and feeding of the columns were made daily. The pH of the columns was recorded daily as a simple monitoring test. More extensive analyses were done less frequently.

Each set of columns was operated under different conditions. Group 1 was closest to common treatment procedure in that the sample was neutral-

FIGURE 2. DAILY pH MONITORING OF LAGOON SIMULATION UNITS



ized to pH 7 with sodium hydroxide. Group 2 was also neutralized to pH 7, but salt was added to increase salinity by about 15%, thereby simulating possible conditions resulting from a water conservation program. Group 3 was fed fed with sample neutralized to pH 5.5.

All feed was supplemented with nitrogen and phosphorus. For an initial BOD of 2500 mg/l, total P of 4.6 mg/l and total N or 46.1 mg/l, a BOD:N:P ratio to 100:50:1 was obtained by an addition of 20 mg/l as P and 80 mg/l as N to the samples.

Results of the treatability study show that adequate aeration is essential to achieve biological treatment. As indicated in Figure 2 the pH was highly dependent on the air supply. When the experiment was begun using diffuser to disperse air in the column the pH dropped because of inadequate dissolved oxygen. After the diffusers were replaced with pipettes, allowing an increase in air supply, the pH increased above neutrality, During the course of the experiment whenever the air supply decreased for any reason the pH fell drastically, illustrating the need for an adequate, dependable air supply to support aerobic biological attack on organic acids in the wastes. Increase in aeration soon led to improved pH in the system, sometimes assisted in the initial recovery by addition of sodium bicarbonate.

Our original hypothesis was that there would be a significant difference between treatability at pH 5.5 and at 7.0. This was not observed. In fact, the system increased in alkalinity after biological activity began. Thus despite the different initial pH, all cylinders stabilized around a pH of 8.0. This also is shown in Figure 2.

As shown by averages in Table 7 the BOD removal beyond 30 days was not substantial. Thus, '-he existing lagoon should be able to handle hydraulic beyond its design capacity. Another implication is that in future study shorter time periods should be adequate. To obtain effluent BOD values lower than those indicated probably will require addition of settling and perhaps other processes in addition to the aerated lagoons.

A 15% increase in salinity did not adversely affect treatment as shown by comparing results of unit 1 and unit 2. Therefore, a substantial water conservation program could be instituted without altering waste treatment. It should be noted that the influent salinity values used in this experiment (12,000 mg/l chloride) should be well above the yearly average.

## Conclusions

1) This pickle plant waste can be treated biologically.
2) Extensive neutralization of the influent may not be necessary to maintain an acceptable pH in the lagoon. Possibly after initial neutralization and stabilization of the biological activity, no neutralization of the influent will be needed. In order to achieve this end, a pH monitor in the first basin would be highly desirable.

TABLE 7A. DATA FROM TREATABILITY STUDIES

| Characteristic | Date 1974 | Pond Influent | Unit No. 1 15 Days | Unit No. 1 30 Days | Unit No. 1 45 Days | Unit No. 2 15 Days | Unit No. 2 30 Days | Unit No. 2 45 Days | Unit No. 3 15 Days | Unit No. 3 30 Days | Unit No. 3 45 Days |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $BOD_5$, mg/l | 4/4 | >2,250 | 120 | <10 | <10 | 50 | <10 | <10 | 90 | <10 | 30 |
| | 4/18 | | 186 | 111 | 57 | 165 | 93 | 114 | 198 | 72 | 45 |
| Total Org. C., mg/l | 2/2 | 1,400 | | | | | | | | | |
| | 2/14 | 1,400 | | | | | | | | | |
| | 2/18 | 1,199 | | | | | | | | | |
| | 2/19 | 1,110 | | | | | | | | | |
| | 2/26 | 1,270 | | | | | | | | | |
| | 3/20 | 2,700 | 200 | 200 | - | <100 | <100 | - | - | <100 | - |
| | 3/28 | | <100 | <100 | - | 200 | <100 | - | <100 | <100 | - |
| | 4/18 | | <100 | <100 | <100 | <100 | <100 | <100 | 200 | <100 | <100 |
| Susp. Solids, mg/l | 2/2 | 235 | | | - | | | | | | |
| | 2/14 | 237 | | | - | | | | | | |
| | 3/20 | 345 | 2,340 | 488 | - | 2,667 | 753 | - | 2,550 | 1,020 | - |
| | 3/28 | | 1,095 | 2,721 | - | 2,990 | 570 | - | 3,690 | 940 | - |
| | 4/18 | | 703 | 333 | 418 | 1,060 | 530 | 560 | 1,350 | 775 | 305 |
| Total Solids, mg/l | 2/2 | 23,600 | | | | | | | | | |
| | 2/14 | 23,970 | | | | | | | | | |
| | 3/20 | 28,240 | 14,380 | 10,670 | - | 15,840 | 13,000 | - | 9,130 | 7,310 | - |
| | 4/18 | | 22,560 | 17,150 | 15,480 | 34,430 | 26,930 | 26,410 | 24,530 | 15,770 | |
| Ammonia, mg/l as N | 2/2 | 9.0 | | | | | | | | | |
| | 2/14 | 8.0 | | | | | | | | | |
| | 2/18 | 8.5 | | | | | | | | | |
| | 2/19 | 7.5 | | | | | | | | | |
| | 2/26 | 6.0 | | | | | | | | | |
| Kjeldahl N, mg/l | 2/2 | 29.0 | | | | | | | | | |
| | 2/14 | 32.0 | | | | | | | | | |
| | 2/18 | 26.5 | | | | | | | | | |
| | 2/17 | 26.5 | | | | | | | | | |
| | 2/26 | 45.0 | | | | | | | | | |
| Nitrite & Nitrate, mg/l | 2/18 | 1.6 | | | | | | | | | |
| mg/l as N | 2/19 | 1.5 | | | | | | | | | |
| | 2/26 | 1.1 | | | | | | | | | |
| Total Phos., mg/l as P | 2/26 | 4.6 | | | | | | | | | |
| Vol. Susp. Solids, mg/l | 4/18 | | 229 | 193 | 222 | 390 | 225 | 80 | 420 | 300 | 195 |
| Chlorides, mg/l | 4/18 | | 14,200 | 11,000 | 10,600 | 17,700 | 13,100 | 12,700 | 15,600 | 10,600 | 9,200 |
| Conductivity, mmhos | 4/18 | | 29 | 21 | 20 | 31 | 28 | 28 | 28 | 22 | 20 |

TABLE 7B. SUMMARY OF TREATABILITY STUDIES

Unit 1. Initial pH = 7.0, Chloride = 12,000 mg/l

| Analysis | 0 Day | 15 Day | 30 Day | 45 Day |
|---|---|---|---|---|
| Avg. TOC (mg/l) | 1,970 | <150 | <150 | <100 |
| Avg. BOD (mg/l) | >2,250 | 153 | 50 | 33 |
| Avg. Susp. Solids (mg/l) | 270 | 1,450 | 1,180 | 420 |
| Avg. $[Cl^-]$ (mg/l) | 12,000 | 14,200 | 11,000 | 10,600 |

Unit 2. Initial pH - 7.0, Chloride = 13,500 mg/l

| Analysis | 0 Day | 15 Day | 30 Day | 45 Day |
|---|---|---|---|---|
| Avg. TOC | 1,970 | <150 | <100 | <100 |
| Avg. BOD | >2,250 | 110 | 50 | 60 |
| Avg. Susp. Soli[illegible] | 270 | 2,240 | 620 | 560 |
| Avg. $[Cl^-]$ | 13,500 | 17,700 | 13,100 | 12,700 |

Unit 3. Initial pH = 5.5, Chloride = 12,000 mg/l

| Analysis | 0 Day | 15 Day | 30 Day | 45 Day |
|---|---|---|---|---|
| Avg. TOC | 1,970 | <150 | <100 | <100 |
| Avg. BOD | >2,250 | 150 | 40 | 38 |
| Avg. Susp. Solids | 270 | 2,530 | 910 | 300 |
| Avg. $[Cl^-]$ | 12,000 | 15,600 | 10,600 | 9,200 |

3) A water conservation program that increases salt concentration will not adversely affect treatment.
4) Unless further studies show differently, screening and nutrient addition should be practiced.
5) The existing lagoon has sufficient detention time for flows significantly greater than the design flow of 100,000 gals/day.
5) Adequate aeration is crucial to treatment.

## WASTEWATER NEUTRALIZATION

Three alkalis were compared for neutralization of the plant wastewater. The purpose of the experiment was to provide a basis for determining the most economical and effective alkali for wastewater neutralization should large quantities be needed in the future, either for initial raising of the lagoon pH or for maintenance of the proper pH once biological treatment has begun.

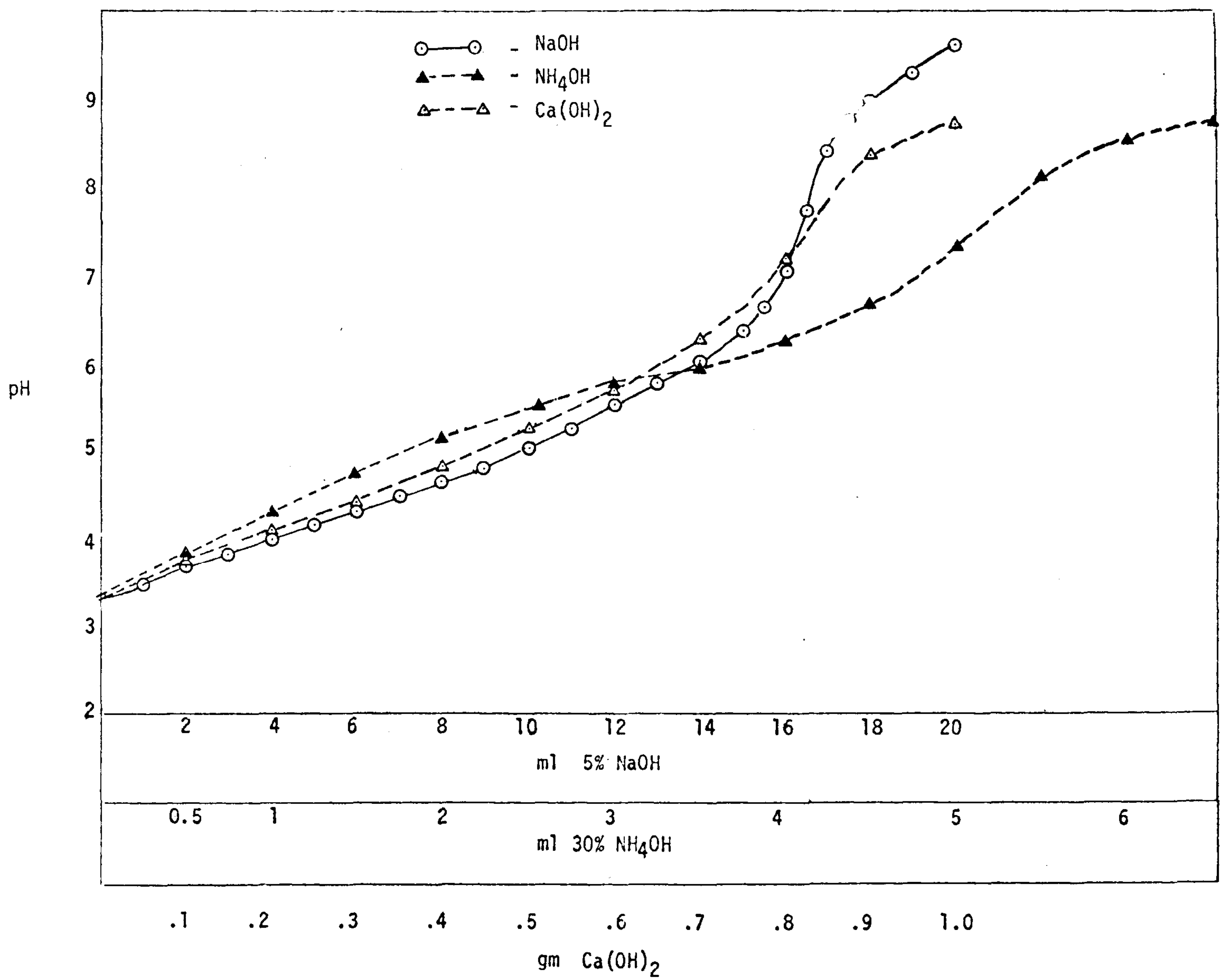
Composite samples (1 liter) of plant effluent were titrated with 5% sodium hydroxide, 30% ammonium hydroxide, or solid calcium hydroxide, which was weighed out in 0.1 gm aliquots that were slurried with distilled water just prior to use. The resulting pH of the plant wastewater was recorded after each addition of alkali.

The titration curves for these bases are shown in Figure 3. Table 8 summarizes the quantities of bases required to neutralize plant wastewater to pH 5.5 and to pH 7.0.

TABLE 8. CHEMICAL REQUIREMENTS FOR NEUTRALIZATION

| pH | NaOH (gals/1000 gals.) | | $NH_4OH$ (gals/1000 gals.) | | $Ca(OH)_2$ (lbs./1000 gals.) |
|---|---|---|---|---|---|
| | 5% | 50% | 5% | 50% | |
| 5.5 | 12.0 | 1.2 | 15.6 | 1.56 | 4.7 |
| 7.0 | 16.0 | 1.6 | 28.8 | 2.88 | 6.6 |

FIGURE 3. TITRATION CURVES FOR UNTREATED WASTEWATER



It should be noted that the above figures are in gals/1000 gals for sodium and ammonium hydroxide, but are in lbs /l000 gals for calcium hydroxide. Availability and cost, in addition to other factors, should be considered before selecting the alkali to use. For example, the possible eutrophic effects of ammonium on the receiving stream, and even the reservoir, must be evaluated carefully before using that base for neutralization.

**Conclusions and Recommendations**

1. If available locally at a competitive price, sodium hydroxide appears to be the chemical of choice because of availability of storage and feed facilities at the site, ease of handling, and minimum precipitate production.
2. Ammonium hydroxide should not be added in excess of nutrient requirements, if any, because of potential downstream eutrophication problems.
3. pH should be monitored in the aeration basin, rather than only in untreated influent waste, to insure adequate control for the biological treatment process.

## RESPIRATION RATE STUDY

Because of the great variability in flows and wastes characteristics, it was important to consider the effects of shock loads upon the biological system. Two types of shocks were considered in this study: low pH and changing salt concentrations.

Effects upon biological activity were noted by changes in the respiration rate of the microorganisms. The procedure followed was in accordance with a technique developed earlier, which has been reproduced in the Appendix. A brief outline of the procedure follows.

Mixed liquor (ML) from several of the pilot lagoon units was mixed and aerated for two days without feeding to allow sufficient time for complete utilization of readily oxidized material. At that point, the endogenous phase of microbial growth had been reached and oxygen uptake was at a minimum (endogenous rate). When material that can be utilized by the organisms is added to a biological system in that condition, an increased rate of oxygen uptake (respiration) is observed. No increase in respiration indicates that the material added is not utilized. A decrease in the respiration rate indicates a toxic effect.

The dissolved oxygen (DO) was measured with a Weston-Stack DO meter using a probe tapered to fit into a BOD bottle. A stop watch was used to measure 1 minute intervals at which time DO was recorded. When DO was plotted against time, a straight line was obtained, the slope of which gave the respiration rate which was compared with the endogenous rate. Since the rate of oxygen uptake depends upon the number of organisms present, the respiration rate was calculated as mg/l of oxygen used per minute per gram of suspended solids. The suspended solids indicated the relative number of organisms present. In this way, rates can be comparable between runs, in spite of different suspended solids values.

The BOD bottle held 300 ml. Twenty ml of feed (a composite sample as in the treatability study) was added and then the bottle was filled with the aerated mixed liquor, To examine pH effects, the pH of the feed solution was reduced by addition of HCl and respiration rate measured at each value. Initial and final pH values were measured for each run, hut no change was observed during the rate measurements.

The mixed liquor plus the feed had a Cl' content of 13,O0O mg/l. To increase salinity, NaCl was dissolved in the feed prior to addition of the ML. To see whether decreased salinity would have a beneficial effect, a 1:2 dilution was made of both ML and feed, This also decreased the suspended solids by half. Nevertheless, data comparison and interpretation were feasible because of calculating respiration rates as mg/l DO per gram of suspended solids, or as percent of endogenous rate.

The mixed liquor had been acclimated to a pH of 6.9 and Cl- concentration of 13,000 mg/l. Figure 4 shows the changes in respiration rate when fed samples of other pH. It is seen that the respiration rate decreases with decreasing pH of the shock load. However, it should be noted that even at the lowest pH (1.5), the respiration rate still was higher than the shocks of low pH. That is not to say that such pH levels could be sustained indefinitely without detrimental effects. pH levels near neutrality allowed maximum utilization of oragnic material, which is most desirable in waste treatment.

Figure 4 also shows effects of changing the salinity. While increasing the salt concentration did reduce the respiration rate, it remained above the endogenous rate. Decreasing the salinity by half had neither a harmful nor beneficial effect upon biological activity. Again, it is important to note that this study shows acute effects due to shock loads and not long term effects, which may be either more or less serious under various circumstances.

## Conclusions

1. The microorganisms are very resistant to low pH shock loads. Wastes should be neutralized to maintain generally desirable pH throughout the system and acceptable effluent pH, without major concern about shock loadings of short duration.
2. Increased salinity does not have a greatly detrimental effect initially. Although further study on long term effects is necessary, water conservation programs should not be delayed for fear of harmful effects to the aerated lagoon by the resulting increased salinity.

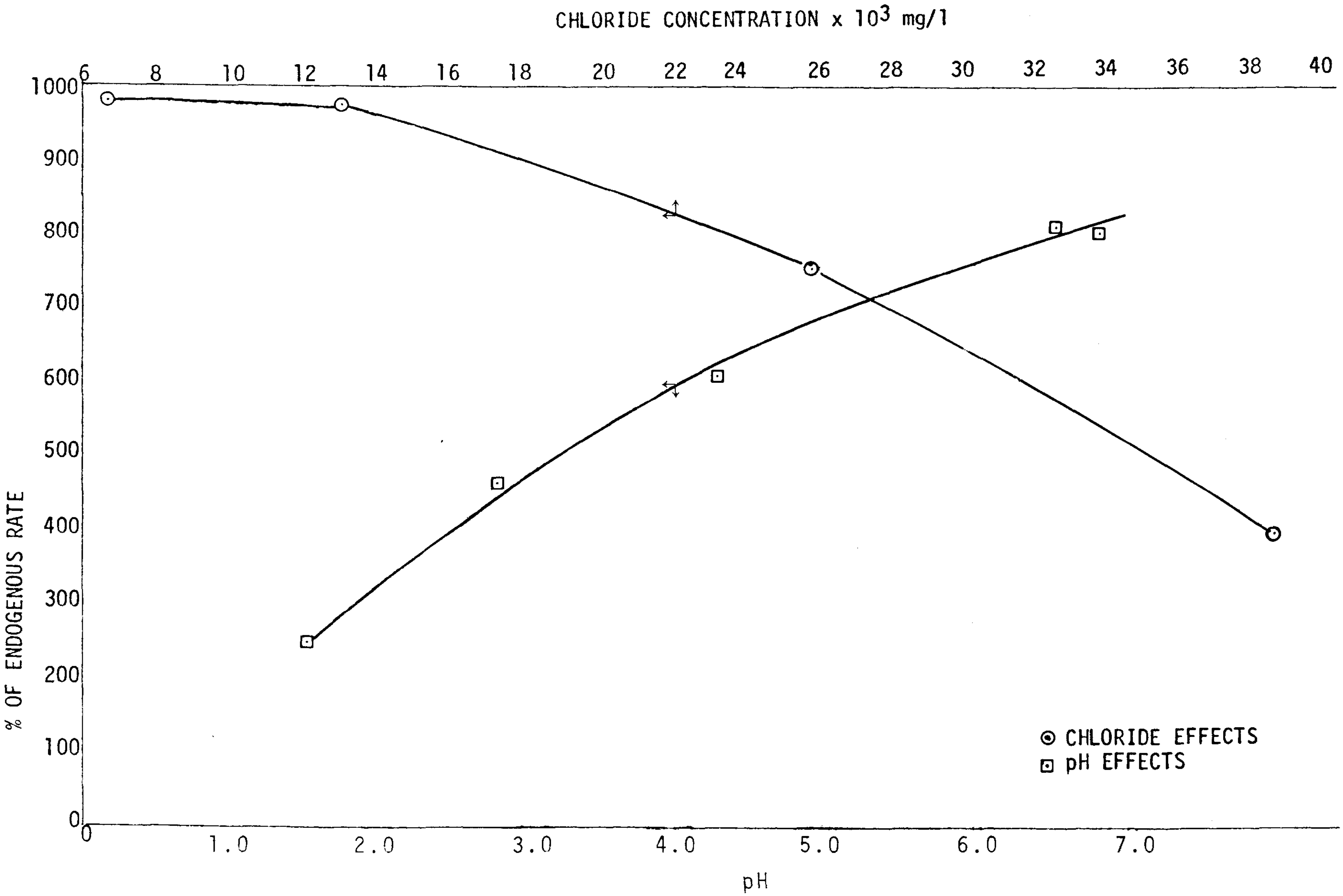



FIGURE 4. EFFECTS OF LOW pH AND HIGH SALT SHOCK LOADING UPON RESPIRATION

## Conclusions

1. The microorganisms are very resistant to low pH shock loads. Wastes should be neutralized to maintain generally desirable pH throughout the system and acceptable effluent pH, without major concern about shock loadings of short duration.
2. Increased salinity does not have a greatly detrimental effect initially. Although further study on long term effects is necessary, water conservatior programs should not be delayed for fear of harmful effects to the aerated lagoon by the resulting increased salinity.

## SUMMARY OF CONCLUSIONS AND RECOMMENDATIONS

1. A consulting engineer should be retained and detailed studies continued.
2. Water flows to each manufacturing process should be metered.
3. Suspended solids should be reduced by repairing floors and otherwise improving dry cleanup procedures, improving maintenance of screens, and removing or recovering suspended matter from the relish operation.
4. Improved screens should be installed at the lagoon influent and better maintenance, routines established.
5. Erosion from the tankyard area should be reduced.
6. Effluent from the manufacturing plant can be treated biologically.
7. pH should be monitored in the first bay of the aerated lagoon.
8. After establishing satisfactory biological activity it may not be necessary to add alkali continuously.
9. Subject to further studies, nutrients (nitrogen and phosphorus) should be added to insure BOD:N:P ratios of 100:5:1.
10. Adequate aeration is essential for successful biological treatment.
11. The existing 1agoon has sufficient detention to provide a high degree of BOD removal for “lows significantly greater than 100,000 gal/day.
12. Microorganisms involved in treatment of this wastewater appear to be resistant to low pH and variable chloride shock loads.
13. Water conservation can be undertaken without fear of significant harmful effects to biological treatment through increased salinity within the range which probably will be encountered in practice.
14. Communications with plant personnel concerning company policies and implementation of wastewater control procedures should be enhanced.

## APPENDIX B

# COST OF PICKLE BRINE RECOVERY

by

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*Based upon a conceptual model of pickle manufacture that delineates waste streams, their rates, and their* **concentrations,** *costs have been estimated for several processes for salt concentration and* **for** *organic removal.*

*Based upon these estimates, reverse osmosis, butane freezing, distillation, and submerged combustion evaporation are most economical for salt concentration; biological oxidation is more economical for organic removal.*

## OUTLINE

## 1.0 A CONCEPTUAL MODEL OF PICKLE MANUFACTURE

In the manufacture of cucumber pickles, a large portion of the cucumber harvest must be preserved for processing at a later time. This preservation is normally accomplished by diffusing salt into the cucumbers. To accomplish this, the cucumbers are normally soaked in strong brine solutions, with periodic replacement of salt to maintain sufficient driving force for diffusion. A reasonable goal is to introduce salt into the cucumbers to the level of 15 percent or so, approximately 0.188 lb salt/lb of cucumbers.

Subsequently, most of this salt must be removed from the cucumbers by processing room: prior to packing.

### 1.1 TANK-YARD PROCEDURES

It is assured that salt is introduced into the pickles in the following staged process. First, pickles are soaked in saturated brine until equilibration; second, a small amount of depleted brine is withdrawn to make room for saturated brine addition; third, equilibration proceeds; and fourth, the process is repeated.

At stage by immediately following brine addition, there are

$c_n$ lb salt/lb cucumbers within the cucumbers, and $w_n$ lb salt/lb water in

the brine. Then denoting the n-plus-first stage as that resulting after equilibration, the salt concentration in the cucumbers will equal that in the brine, thus,

$$c_{n+1} = W_{n+1} = \frac{c_n + w_n}{2}$$

(The voidage within the cucumbers is taken as 50 percent so that there exists, in normal processing, approximately 1 pound water/lb cucumbers).

At this point $d_{n+1}$ lb of water are withdrawn to make room in the tank for the addition of another $d_n$ +l lb of water containing salt near the saturation point. Then $w_{n+1}\ d_{n+1}$ lb of salt are withdrawn from the vessel, and $Bd_{n+1}$ lb of salt are ad ded to the vessel as nearly saturated brine, where B is the replacement brine concentration in lb salt/lb water.

After the addition of concentrated brine, the salt content within the tank is $w_{n+1} - w_{n+1}\ d_{n+1} + Bd_{n+1}$. This expression is to be set equal to s, the interstage concentration to which the salt solution must be adjusted for effective pickle processing. Solving for $d_{n+1}$, there results

$$d_{n+1} = \frac{s - w_{n+1}}{B - w_{n+1}}$$

These formulas can be used to calculate step-wise through the pickle salting procedure. Assume $d_0 = 0$, $w_0 = 0.194$ lb salt/lb water,

s = 0.194 lb salt/lb water, and B = 0.33 lb salt/lb water (0.194 lb salt/lb water corresponds to 16.25 per cent salt, and 0.33 lb salt/lb water corresponds to 25 percent salt). Stage-wise concentrations are the following:

| | |
|---|---|
| $C_0 = 0$ | $S = 0.194$ |
| $W_0 = 0.194$ | $B = 0.333$ |
| $C_1 = W_1 = 0.097$ | $D_1 = 0.411$ |
| $C_2 = 0.097$ | |
| $W_2 = 0.194$ | |
| $C_3 = W_3 = 0.1455$ | $D_3 = 0.259$ |
| $C_4 = 0.1455$ | |
| $W_4 = 0.194$ | |
| $C_5 = W_5 = 0.170$ | $D_5 = 0.147$ |
| $C_6 = 0.170$ | |
| $W_6 = 0.194$ | |
| $C_7 = W_7 = 0.182$ | $D_7 = 0.079$ |
| $C_8 = 0.182$ | |
| $W_8 = W_9 = 0.188$ | Assume STOP |

Since 0.188 lb salt/lb cucumber is the target salt concentration within the cucumbers, the cucumber salting process is halted at this point.

Per pound of salt stock, the spent brine withdrawals from the processing tanks at the various stages are the following, with totals as shown.

Per pound of salt stock, get the following:

| | | |
|---|---|---|
| | 0.411 lb $H_20$ | 0.0399 lb salt |
| | 0.259 lb $H_20$ | 0.0377 lb salt |
| | 0.147 lb $H_20$ | 0.0250 lb salt |
| | 0.079 lb $H_20$ | 0.0144 lb salt |
| With Totals | 0.896 lb $H_20$ | 0.177 lb salt |
| + | 1.00 lb stock | 0.188 lb salt |
| | | 0.493 lb salt |

Thus, per pound of cucumbers, the draw-down from the tanks is 0.896 lb water containing 0.177 lb salt or 0.131 lb salt/lb water. In addition, there is l-lb water remaining in the tank containing 0.188 lb salt.

Assuming that 500,000 bushels of cucumbers are processed in 100 days during the salting down season, and assuming furthermore 9 gal/bushel cucumbers and 4 lb/gal, the estimated weight of cucumbers is 18 x 106 lbs. At 0.896 lb water/lb cucumber, the water rate is then 16.1 million lb/l00 days or approximately 19.4 thousand gal/day.

The initial concentration is 0.131 lb salt/lb water, which corresponds 7.63 lb water/lb salt. This stream is to be concentrated to 0.33 lb salt/lb water, or 3.0 lb water/lb salt. Consequently, the fraction $\frac{4.63}{7.63}$ = 60.7 percent of the water must be removed in effecting this separation. Thus the water removal rate in processing the tank yard brines is $1.21 \times 10^6$ gal/100 day season, or 12,000 gal/day.

The final brine solution from which the cucumbers are withdrawn for processing contains 0.188 lb salt/lb water. This brine is sufficiently concentrated that it needs no further processing and can be saved as is until the next season. It is assumed that this brine is stored in the tanks until the following season at which time it is reconcentrated with saturated brine to begin processing the new crop.

1.2 PROCESSING ROOM PROCEDURES

It is assumed that in salt removal, each lb of cucumbers containing 0.188 lb salt is contacted with 2-lb of water and allowed to equilibrate. After equilibration there results l-lb of cucumbers containing 0.0626 lb salt and 2-lb water containing 0.125 lb salt. This dilute brine stream constitutes the first processing waste.

The lb of cucumbers is washed a second time with l-lb of water. Sufficient time for equilibration is not allowed, however; the washing process is stopped at the point at which the cucumbers contain 0.038 lb salt/lb cucumbers. The dilute water stream from this washing containing 0.025 lb salt/lb of water is the second processing waste. [The figure 0.038 lb salt/ lb cucumbers represents an average salt concentration weighted according to the relative production of dills and sweets. We have assumed 60 percent dills (4.7 percent salt) and 40 percent sweets (2.5 percent salt). The weighted average gives 3.82 percent salt remaining in the pickles or 0.038 lb salt/lb cucumbers.]

The rate of first processing waste, based upon an assumed 200 days of operation, is 21,600 gal/day containing 0.0626 lb water/lb salt. In brine recovery, the stream must be concentrated to 3 lb water/lb salt, or 17,500 gal/day of water must be removed, leaving 4,100 gal/day of brine at a salt level of 0.33 lb salt/lb water.

Similarly, the rate of second processing waste is 10,800 gal/day containing 40 lb water/lb salt. This stream must be concentrated to 3 lb water/lb salt; thus, approximately 10,000 gal/day of salt free water must be removed to leave 800 gal/day of brine with concentration 0.33 lb salt/ lb water.

A schematic diagram of these streams along with the flow rates and compositions is given in Figure 1.

## 1.3 BRINE CONCENTRATING REQUIREMENTS

Comparing water removal rates, i.e., 12,000 gal/day from the tank yard brines versus a total of 27,500 gal/day from processing room waste, indicates that equipment sized to handle the latter could easily handle the former. Thus, attention is given to the design of equipment to handle mixed processing room wastes delivered at a rate of 32,400 gal/day containing 0.092 lb salt /lb water. Separating equipment must be sized to remove 27,500 gal/day of water leaving 4,900 gal/day of saturated brine to be used in subsequent processing.

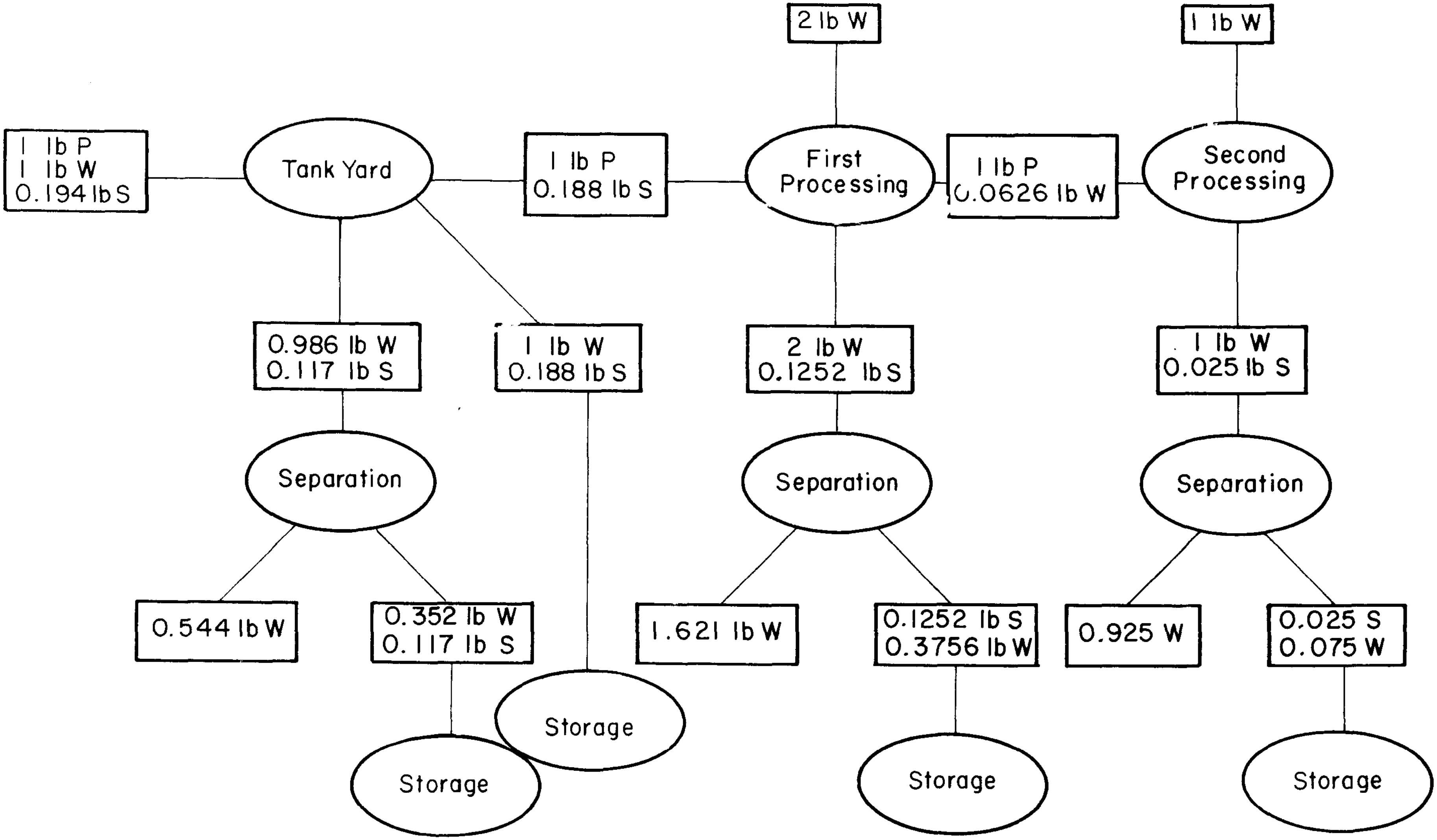


FIGURE 1. Schematic of Stream Flows in Pickle Processing. Basis: 1 lb Pickles

## 2.0 METHOD OF COST ESTIMATION

Costs have been estimated using a slight modification of a method developed by the Office of Saline Water[1] in which overall process costs are based on the costs of the major pieces of equipment. The cost of the major pieces of equipment must be estimated from vendor quotes, from the literature, or from other means of determination, and costs other than those for major equipment are taken as fixed percentages of the major equipment costs.

Total annual operating costs of a plant are comprised of

1) Capital costs, including major equipment, other materials, construction labor, indirect labor, taxes, insurance, engineering, and interest on construction capital, and
2) Annual operating costs, including the amortized capital cost, interim replacement, taxes, insurance, operating labor, and overhead. The total annual operating costs can, if desired, be expressed as the total cost per unit of production. In the case of pickle brine processing, significant bases for report cost/unit of production might be total cost per ton of pickles or total cost per ton of salt recovered.

### 2.1 CAPITAL COST ESTIMATION

Capital costs are estimated as follows:

Assuming that a process schematic has been drawn and that major items of equipment have been specified and their size determined, costs are estimated for these major items of equipment; these costs are designated as E.

In the construction of-the plant, other materials must also be purchased, piping, electrical wiring, small pumps, instrumentation, etc. These costs are referred to as other materials costs, M, and are taken as 40 percent of E.

Labor must be provided for construction of the plant. Construction labor, L, is taken as 60 percent of E.

[1]Jenkins, David S. et al., "A Standardized Procedure for Estimating Costs of Saline Water Conversion", Office of Saline Water, March 1956.

Labor indirect charges, including payroll burden, supervision, and construction equipment, is 43 percent of the labor charges, or has 25.8 percent of the major equipment charges.

The sum of these four costs is designated as the basic plant cost (BASC) and is equal to 2.258 times the major equipment cost.

To the basic cost must be added engineering cost, (12 percent of the basic plant cost), and tax and overhead (12 percent of the sum of the basic plant cost plus engineering charges) to get the fixed capital investment (FCI).

Working capital and startup funds at 11 percent of the fixed capital investment must also be included as must interest on the construction capital at 5 percent of the fixed capital investment.

The total of all these charges gives the total capital investment. A sumnary of the factors entering into the total capital investment is given in Table 1.

## 2.2 OPERATING COST ESTIMATION

Annual operating costs are based, by and large, on the total capital investment. First, the fixed costs (capital recovery, replacements, taxes, and insurance) as a fraction of the total capital investment are calculated. Assuming 8 percent for 15 years, the capital recovery factor is 0.117, or 11.7 percent of the total capital investment must be set aside each year for capital recovery. To this must be added insurance at 0.3 percent, state and local taxes at 6 percent and a fund for replacements at 0.4 percent. Summing these items gives the total fixed cost at 0.184 times the total capital investment. To these fixed costs must be added direct operating costs consisting of operating labor plus maintenance labor and supplies. For pickle processing it is assumed that no supplementary charges must be taken for labor, in other words, that labor requirements can be met by existing staff. Maintenance labor and supplies are taken to be 4 percent of the total capital investment.

Adding plant overhead at 2 percent of the total capital investment gives the total annual cost as 0.244 times the total capital investment.

To these costs must be added annual cost for energy, but credit can also be taken for the value of salt recovered.

The total annual cost so estimated should include all cost centers and should reasonably form the basis for initial estimates of process feasibility and of process economic attractiveness.

A sumnary of factors entering into annual operating costs is given in Table 2.

TABLE 1. CAPITAL COST ESTIMATION

| | | | | |
|---|---|---|---|---|
| Major Equipment Cost, E | | | | |
| Other Materials Cost, M | | 0.4 E | | |
| Construction Labor, L | | 0.6 E | | |
| Labor Indirect | | 0.43 L | = | 0.258 E |
| | = | BASC | = | 2.258 E |
| Engineering: 0.12 BASC = BARC | | | = | 0.2710 E |
| Tax (2% BARC, OH 10% BARC) | | | = | 0.0325 E |
| | = | FCI | = | 2.562 E |
| Working Capital and Startup: 11% FCI | | | = | 0.282 E |
| Interest on Construction Capital = 0.5 FCI | | | = | 0.141 E |
| | | TOTAL | | 2.985 E |
| | | TOTAL (FCI) = | | 3.0 E |

## 3.0 COST ESTIMATES FOR BRINE CONCENTRATION

Costs have been estimated for the following processes for recovering salt from pickle brines: reverse osmosis, electrodialysis, two freezing processes - vapor compression and butane, solar humidification, solar distillation, the following methods of distillation; multi-stage flash, long-tube vertical, vapor reheat, and vapor compression; and submerged combustion evaporation.

TABLE 2. ANNUAL OPERATING COSTS

| Fixed Costs | | Fraction of TCI |
|---|---|---|
| Capital Recovery | | 0.117 |
| Insurance | | 0.003 |
| Taxes | | 0.060 |
| Replacements | | 0.004 |
| | TOTAL | 0.184 FCI |
| **Direct Costs** | | **Fraction of TCI** |
| Labor - assume existing staff | | 0.04 TCI |
| Maintenance labor and supplies | | |
| **Indirect Costs** | | **Fraction of TCI** |
| Plant Overhead (Total Indirect) | | 0.02 TCI |
| | TOTAL ANNUAL COST | 0.244 TCI |

Costs for major items of equipment for these processes have been estimated in a previously published study[2] for relatively large-scale plants. These major equipment costs were scaled to the problem in question, first, by using the exponential rule $C_1/C_2 = S_1/S_2 0^{0.7}$ to correct for the smaller scale associated with pickle manufacture, and second, by multiplication by the Marshall Stevens Construction Cost Index Ratio, to convert 1965 construction dollars into 1973 dollars.

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[2] De La Rue, R. E., and Jones, J. M., "Comparative Engineering Analysis of Alternative Processes for Saline Conversion", Prepared for Office of Saline Water, U. S. Dept. of the Interior, Washington, D. C., under Contract No. 14-01-0001-412, May 1966.

These estimates have been validated by selected cross-checking. Selected types of equipment, especially evaporators, are the subject of independent cost correlations. These evaporators costs are calculated for processing and compared with evaporator contributions to the total cost as calculated using the OSW method, These results were in substantial agreement.

Cost estimates are summarized in Table 3. Reverse osmosis, butane freezing, distillation, and submerged combustion evaporation seem to warrant further consideration.

## 4.0 COST ESTIMATES FOR ORGANIC REMOVAL

Estimates have been made of the cost of two processes for the removal of organic materials from pickle brine: submerged combustion evaporation followed by kiln drying, and biological oxidation.

For the submerged combustion process, it has been assumed that submerged combustion would also be used for salt concentration, consequently the evaporator cost has been estimated as an increment to the evaporator cost for salt concentration.

Costs of biological oxidation have been estimated from published information,[3] assuming that BOD removal proceeds by first order kinetics and that the costs would be identical to those for municipal waste treatment providing the residence time is increased to account for the higher BOD in pickle brines. Under these assumptions, the time required for oxidation of BOD at a concentration of 4000 mg/liter is 2.3 times the time required for oxidation of 200 mg/liter, taken as representative of municipal sewage. Thus, the plant size should be 2.3 times 25,000 gal/day or about 63,000 gal/day. Total capital investment estimates were based on this size plant.

Cost estimates for organic removal are summarized in Table 4.

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[3]Smith, R., "A Compilation of Cost Information for Conventional and Advanced Wastewater Treatment Plants and Processes, Prepared for Federal Water Pollution Control Administration, Cincinnati, Ohio, 1967.

## TABLE 3. COST ESTIMATES FOR CONCENTRATING PICKLE BRINE

| | Major Equipment Capital Cost for Brine Processing | | Total Capital Investment in 1973 Dollars $ x $10^3$ | Total Annual Cost $ x $10^3$ | Estimated Annual Power Cost $ x $10^3$ | Estimated Annual Fuel Cost $ x $10^3$ | Total Annual Cost Including Fuel and Power $ x $10^3$ |
|---|---|---|---|---|---|---|---|
| | 1965 Dollars $ x $10^3$ | 1973 Dollars $ x $10^3$ | | | | | |
| Reverse Osmosis | 56 | 80 | 240 | 59 | 1.7 | -- | 61 |
| Electrodialysis | 360 | 514 | 1,542 | 554 | 16.1 | -- | 550 |
| Freezing | | | | | | | |
| Vapor Compression | 78 | 111 | 333 | 81 | 8.8 | -- | 90 |
| Butane | 70 | 100 | 300 | 73 | 1.8 | -- | 75 |
| Solar | | | | | | | |
| Humidification | 143 | 204 | 612 | 149 | 2.0 | -- | 151 |
| Distillation | 129 | 184 | 552 | 135 | 0.05 | -- | 135 |
| Distillation | | | | | | | |
| Multistage Flash | 57 | 82 | 246 | 60 | 0.1 | 3.4 | 64 |
| Long Tube Vertical | 57 | 82 | 246 | 60 | 0.2 | 3.9 | 64 |
| Vapor Reheat | 76 | 109 | 327 | 80 | 0.1 | 3.0 | 83 |
| Vapor Compression | 130 | 186 | 558 | 136 | 0.4 | 2.7 | 139 |
| Submerged Combustion Evaporation | -- | 65* | 195 | 48 | -- | 23 | 71 |

*Vendors quote

TABLE 4. COST ESTIMATES FOR ORGANIC REMOVAL FROM PICKLE BRINE

| | Equipment Cost $\$ \times 10^3$ | Total Capital Investment $\$ \times 10^3$ | Total Annual Cost $\$ \times 10^3$ | Fuel Cost $\$ \times 10^3$ | Total Annual Cost $\$ \times 10^3$ |
|---|---|---|---|---|---|
| Submerged combustion and incineration | 35[4] | 105 | 25 | 7 | 32 |
| Biological oxidation (activated sludge) | | 60[5] | 15 | | 15 |

[4]Chilton, C. H., Cost Engineering in the Process Industries, McGraw-Hill Book Co., New York, 1960.

[5]Smith, R., "A Compilation of Cost Information for Conventional and Advanced Wastewater Treatment Plants and Processes", Prepared for Federal Water Pollution Control Administration, Cincinnati, Ohio, 1967.