REPORT ON ION-EXCHANGE PILOT PLANT - ALVARADO
1946 CAMPAIGN

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After the small pilot plant operation during the 1945 campaign, it was decided to construct a larger pilot plant for operating during the 1946 campaign. This was a cooperative venture with the American Cyanamid & Chemical Co. (after August 1, 1946, this company was absorbed by, and assumed the name of, its parent company, the American Cyanamid Co.) Two contracts were signed —one covering construction and operation of the pilot plant; and the other, licensing later full scale operation under patent applications owned by Cyanamid. According to the pilot plant contract, Cyanamid furnished all equipment and construction material, except the building and certain outside tanks, while Holly furnished construction labor, building, and miscellaneous equipment. Holly also furnished all operating supplies such as caustic, acid, raw juice, water, steam, etc. Cyanamid furnished a generous number of technical men and three experienced chemical operators, while Holly furnished three analysts and various common labor.

No sugar end was provided for the pilot plant, since it was agreed that no problems serious enough for pilot plant investigation would be encountered in producing a marketable sugar from a clear thin juice of high purity. Effluent juice from the pilot plant could re-enter the main process at First Carbonation, Second Carbonation, or the thin juice boiler, if the juice was of acceptable quality.

DESCRIPTION OF EQUIPMENT

Building - 40x70' galvanized iron building with concrete foundations and floor, so constructed that the floor may later be raised and the building used as a bag warehouse.

Ion-Exchange Unit - Eight columns—4 anion and 4 cation—6'0" dia. x 10'0" high, rubber lined, both heads dished. Bottom dish filled with concrete, to support under-drains, and surfaced with corrosion resistant materials. Under-drains are a number of nozzles located over the bottom and connected to bottom outlet. Above the under-drains there is one foot of sized anthrafilt (leached anthracite coal), above which is the resin bed. The resins used are manufactured by the American Cyanamid Co. The cation resin is Ionac C-200 while the anion resin is Ionac A-293-M. The overdrain consists of perforated 4" pipe located above the top resin level. The top of the column is closed by a manhole cover which contains the back wash drain and safety valve.

Each column has a bottom connection to the under-drains, a side connection to the overdrain and a top connection to the sewer. All juice and water piping are 4" and mostly rubber-lined pipe to prevent corrosion. Each column has a regenerant line—cation columns have lead lines for acid regenerant while the anion columns have iron lines for caustic. Valves are of the Hills-McCanna (Saunders Patent) type and rubber lined. Two water valves on

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each column allow either up or down flow of water. Raw juice may be made to enter any cation column and sweetwater or effluent juice may be removed from any anion column. Across the front of the units are the following headers: Raw juice, sweet water, effluent juice, return line, and the lead acid line. At the back of the columns are the water and caustic headers.

Weigh Tanks. Juice is weighed in and out of the pilot plant in four weigh tanks--two for influent and two for effluent. The tanks are 4'4-5/8" diameter x 7'6", equipped with a bubble tube. Foxboro juice scales, similar to our raw juice scales, weighed the juice and operated the weigh tanks. The weigh and bumper tank installation is for pilot plant use only and would not be included in a large scale plant.

Caustic System. 48 per cent liquid caustic was brought to the plant by tank car and air unloaded into two discarded crystallizers (12,000-gallon capacity) set up near the unloading spur. From this storage the caustic was pumped into a dilution tank, 5'6" diameter x 5'0" high, in which the caustic was diluted to about 25 per cent. From this tank the 25 per cent caustic is pumped to the columns by two water eductors (same principle as a boiler injector). The eductors; besides pumping the caustic, also dilute it to the desired 4-6% The pounds of caustic used were measured by the inches of 25 per cent caustic removed from the tank.

Acid System. 93 per cent sulfuric acid was air unloaded from tank cars into a 7000-gallon discarded tank car set up as a storage tank. Acid from this tank was pumped by a duriron pump to the dilution tank in the pilot plant. (No special piping or lining is required for concentrated sulfuric acid.) The acid dilution tank is a lined steel tank 8'3" diameter x 6'6" high--covered and vented. Lead cooling coils are provided to remove the heat generated by the dilution. The rate of flow of dilution water and acid are measured by rotameters so that approximately 25 per cent acid results from the dilution. The dilute acid is then withdrawn to a smaller lead lined measuring tank, 4'6" diameter x 4'0" high, and pumped to the columns by eductors. As in the case of caustic, the concentration of acid to the columns is 4-6% and the pounds of acid used are determined by the inches withdrawn from the tank.

Juice Coolers. Two juice coolers of 240 and 460 sq. ft. area were provided in the factory to cool raw juice from battery temperature to the operating temperature. Later a third cooler of 1760 sq. ft. surface was added. These coolers gave insufficient cooling and were of the wrong type, but were the only ones available. Well water at about 20 deg. C. was used to cool the juice.

Instruments. The following instruments were installed and used:

1 - 4-point Leeds & Northrup resistance meter with cells in effluent from each column. Cell constant = 0.2. Meter range 0 to 20000 ohms in two scales.

1 - 4-point Leeds & Northrup pH meter, glass electrodes, one point on each cation effluent.

1 - Ring balance flow meter on raw juice to columns.

2 - Foxboro juice scales for recording and controlling influent and effluent juice tanks.

1 - Flame photometer for measuring sodium and potassium.

Water meters on water to columns, water for acid and caustic regenerant tanks, and sweetwater.

Valve indicators, indicating turns open on all juice, water, and regenerant valves.

GENERAL CONSIDERATIONS

The history and the chemistry of ion-exchange have been very ably described in numerous papers previously and will not be repeated here.

There are several methods of operating an ion-exchange installation, such as the unit at Alvarado. The plant was designed to operate on a practically continuous basis, or "merry-go-round"; that is, three pairs of cells are operated in series. As the oldest pair, taking raw juice, becomes loaded with impurities, it is taken off the line and a fresh pair is added to the effluent end. The former middle pair then becomes the first pair. The pair removed from the line is sweetened off through the unit, regenerated and sweetened on one cycle later as the final pair.

The other method of operation is not continuous and is called "series operation." In this method, six beds (three pairs) are operated in series until the juice coming from the last pair drops below a predetermined purity at which point the entire six beds are sweetened off and regenerated as above. It can be seen that in the commercial application, at least two sets of six beds would be necessary in order to process juice continuously..

The pilot plant started the first day of campaign, September 17, 1946, and operated more or less continuously throughout the beet cutting season. After starting the pilot plant, an additional 1760 sq. ft. cooler was installed to reduce the temperature and consequent formation of invert. In all, forty-four days of operation were realized, mostly devoted to merry-go-round operation, with a few days spent in investigating series operation.

During the entire campaign, mixing unclarified ion-exchange effluent with the factory juice stream resulted in the formation of some color in thick juice. This color evidently was the result of decomposition of invert sugars in the presence of high pH. Unclarified effluent juice, in several tests of mixing with first carbonation juice, formed more color than that found by adding an equivalent amount of pure invert sugar. This additional color formation was later found to be due to the presence of a small amount of pectin in the juice, which decomposes and forms color in high pH. The above is a pilot plant problem and applies only when carbonation juice and ion-exchange juice are mixed. Two points should be emphasized, however: First, that ion-exchange juice is more sensitive to high pH than juice resulting from the conventional process (this means that pH's in an ion-exchange factory would be substantially neutral); and, second, any commercial installation must be completely either ion-exchange or carbonation and not a mixture of the two.

As has been indicated above, the untreated effluent from the columns is of very high purity but still has a definite raw juice colored haze which must be removed before going to the evaporators. The plant was originally designed to remove these impurities by filtration. This was attempted and found difficult. The filtrate from the presses may be clear for a short time but as the pH changes, the haze is often more pronounced than in the original unfiltered juice due to resolution of the cake.

Attempts were made to clarify the effluent juice by use of phosphoric acid and lime in much the same manner as clarification is carried on in a cane refinery. This method was investigated and found to be suitable, although it demands close control and is, at present, quite expensive.

Shortly before the end of operations, clarification with different chemical compounds was attempted and some were found to produce a very clear water white juice. These compounds produce a floc, carrying down the impurities, and the juice settles quite rapidly. Filtration tests indicate that an acceptable flow rate may be obtained. In both the above methods, flocculation may be accomplished in a pH range of 7.0-7.5, and enough soluble material remains in the juice to give sufficient buffer action. If the effluent juice were not clarified, it would probably be necessary to buffer it by addition of a small quantity of a material like a phosphate buffer.

OPERATION

Referring to Fig. 1, the schematic piping layout of the unit, there are eight columns alternately cation and anion, each piped as shown. In the merry-go-round system, six cells are operated on juice at once. For example, raw juice enters No. 7 cation cell, through No. 8, through the return line, and through Nos. 1, 2, 3, and leaving through the effluent valve of No. 4. As Nos. 7 and 8 become exhausted, the raw juice is closed on No. 7 and the water valve is opened, thus sweetening off Nos. 7 and 8. At the same time, Nos. 5 and 6 are sweetened on. Sweetening on water is sewered below 1 brix, sent to the sweetwater tank to 5 brix. and collected as effluent above 5 brix. As soon, then, as the effluent from No. 8, in sweetening off, reaches 5 brix, it is sent to the sweetwater tanks and raw juice is turned on No. 1. Likewise, the effluent from No. 6 (the newly added pair) is sent to the sweetwater tank and finally to effluent. It should be noted that, although flow of juice through the columns is continuous, neither influent nor effluent juice flows continuously.

The juice is now entering column No. 1 and leaving No. 6. Nos. 7 and 8 are exhausted and have been sweetened off. They are now full of water. In order to regenerate them and have them ready to go on the line by the time Nos. 1 and 2 are exhausted, the following procedure is used. The first operation is backwashing, which may be accomplished by running water upflow through the resins and sewering the water from the top of the column. This operation accomplishes two ends. It washes out any mechanically held impurities and it classifies the resin so that minimum pressure drop results later during the juice cycle. The flow rate on backwash is four gallons per square foot per minute and lasts until the backwash drain runs clear. Care must be exercised that the flow rate is not so high that resin is washed over into the sewer.

After backwash is completed, the water valve is closed and after the column is bottom drained to level, it is ready for regeneration. A predetermined amount of regenerant is added and a convenient chart converts this amount into inches to be used from the measuring tank. The eductors are turned on and the regenerant valve at the column is opened, as well as the bottom sewer valve. Regenerant flow is down through the column and out to the sewer. The operation requires about seven minutes for each column or about ten minutes for the pair.

As noted above, regeneration efficiency is quite low, therefore, the spent regenerant may be collected in a separate tank, saved, and re-used. The following table gives some idea of the saving effected:

No Re-use		Re-Use
240	Pounds new Caustic	110
	Pounds used Caustic	130
240	Pounds Total Caustic	240

After regeneration, the next step is rinse, which is accomplished downflow. The cation column is rinsed first and the rinse water is sewered until the pH increases to about 2.0 pH, at which time the rinse water from the cation column is used to rinse the anion bed. Rinsing is continued until the pH of the anion rinse decreases to 10 pH. The anion column is never rinsed with raw water since the magnesium in the water would foul the resins. After rinsing the pair is ready to be put on the line as the final pair. Since, after rinsing during the sweetening on period, the water from the anion column is completely demineralized, it may be saved and used for diluting caustic or other uses. This is an important source of good water for mills with a hard water supply.

It is desirable to use the greatest coordination possible and to use numerous short cuts in reducing the time for these operations to a minimum. The pilot plant capacity increased from 150 to 300 tons per day--mostly due to an effort to coordinate operations.

Both continuous recording pH meters and resistance meters were connected in the effluent line of each column and a conductivity cell was installed in the raw juice line. For a means of determining just when to cut off the first pair and regenerate it, both conductivity and pH control were tried.

The reason for the importance in accurately determining the cut off point lies in the property of ion-exchange resins to exchange weakly ionized materials for the stronger ones. Thus, fresh cation resin holds both sodium and calcium and it becomes saturated with both. At this point calcium begins replacing sodium on the exchanger, so that the effluent contains the original sodium plus an amount equivalent to the calcium held on the exchanger.

Similarly, the anion exchanger leaks acids like carbonic, and various organic-nitrogen acids, which have been replaced by the stronger mineral groups, such as chlorides and sulfates. The compounds which leak first, and cause lowering of resistance and purity, are nitrogen compounds of protein, or amino, structure. Unless the first pair is cut off at the proper point, excessive leakage causes lowered capacity in the middle and final pair. In fact, it is possible to over-run the first pair to such an extent that the purity for a number of cycles remains low.

The table below gives typical ion analysis on raw and effluent juices:

	Raw Juice	Effluent Juice
Brix	12.6	10.1
Sugar	11.15	9.82
Purity	87.6	96.8
Invert Sugar per 100 Bx.	0.7	2.0
Total Sugars	88.3	98.8
Non Sugar Elim.		89.7
Sodium	860	28
Potassium	1615	6
Hardness	1595	40
pH	6.3	8.5
Total Measured Cations	4070	74
Total Measured Anions	4420	54
Ash Elimination		98.5

SPECIFIC CONSIDERATIONS

Water Consumption. It is true that ion-exchange uses a great deal of water. One authority on the subject claims that the proper location for an ion-exchange plant is on the shore of a very large lake. The table shows water consumption broken down into its various uses:

Use	Gal. per Regen.	Gal per Ton Beets
Back Wash	2984	434
Rinse	2400	349
Sweeten Off	2893	421
Diluting Alkali	95	14
Diluting Acid	93	14
Cooling Acid	221	32
Eductors	725	106
	9411	1370

Typical Amounts of Water Used in Pilot Plant Operation.

In a commercial size plant, however, a large amount of this water could be saved/ for instance, mixed rinse water could be re-used for diluting chemicals, cooling and eductors, and some back wash; or the last third of the back wash water could be recycled. With all savings in effect, it is thought that water consumption could be reduced to about 900 gallons per ton beets or, for an 1800-mill, 1,620,000 gallons daily.

Juice Cooling. Raw juice, coming from the battery at about 50 deg. C., should be cooled to around 20 deg. C. to prevent excessive inversion losses. In the pilot plant, this was accomplished by use of multipass tubular coolers using water at about 20 deg. C., which cooled the juice to around 23 deg. C. 125 G. P. M. of cooling water were required. This water was taken from the well water supply and returned to condenser water supply. A great deal of trouble was experienced with bacterial inversion inside the coolers. Cool raw juice, saturated with air, is, of course, a perfect medium for rapid bacterial growth, which was so great that it was desirable to sweeten off the plant and steam sterilize about every six days. Copper sulfate was added to the juice at 2 ppm. and this addition made a noticeable reduction in bacterial activity. In a commercial installation, some water cooling would undoubtedly be used, but both heat and water could be saved by using heat exchangers. The bacterial problem could be solved by installing an extra heat exchanger to be used as others are cut out for steaming. Mills with warm water supplies would undoubtedly be required to install refrigeration equipment to reach the operating temperature. An 1800-ton plant would require forty tons of refrigeration to reduce the temperature of the juice stream one degree C. Proper use of heat exchangers between influent and effluent juices would greatly reduce mechanical refrigeration requirements.

Inversion. The average increase in invert sugar per 100 Bx. for pilot plant operation was 1.43 and the average temperature of influent raw juice was 23 deg. A great deal of this inversion is bacterial and it is felt that it can be reduced to an unimportant amount by eliminating all bumper tanks for cold raw juice, which are ideal breeding places for bacteria. The actual increase in invert sugar at 23 deg. at the cation pH and existing contact time is 0.2. The cation exchanger, however, seems to act as a catalyst for the inversion of sucrose so that the actual increase in invert sugar is 0.5%. By reducing the influent temperature, the inversion rate is reduced. Loss due to inversion can be assumed to be .05 per cent on beets.

Losses. The losses in the pilot plant, calculated from sugar entered less sugar returned were .69 on beets, of which 0.20 was due to inversion. The remaining .49 represented sugar actually lost to the sewer. The raw juice bumper tank and weigh tank were uncovered tanks and thus created a serious foam problem. A great deal of this loss is purely mechanical, due to losses in foam, spills, etc. A very accurate measure of the real ion exchange loss was gotten, however, by sugar analysis of sweetening on and off waters. As in the case of the battery or presses, the loss may be regulated by the amount of wash water used and the proper loss is that which gives minimum costs. In this case evaporation cost was balanced against sugar loss to give the curve shown in Fig. 5. It will be noted that the cost curve (evaporation cost plus value of sugar loss) reaches a minimum which is the point below which to send washings to the sewer.

By sewering wash water at 1 brix, the losses is .04 per cent on beets and the total ion-exchange loss would be .09 on beets; that is, .05 for inversion and .04 on sewer losses.

It is interesting to note that the purity of the wash water does not remain constant throughout the sweetening off; but it slowly decreases to zero. In other words, the sugar washes out of the resin beds faster than other solids. This same phenomenon may be noted in washing down a char filter in a cane refinery.

Dilution. As might be inferred from the sweetening off curves, the dilution and sweet water are an important factor. The water added amounted to 88.1 per cent on beets during the pilot plant operation. A large amount of this dilution is sweet water which can be introduced into the battery at a point of equal brix so that the load on evaporators would not be greatly increased. In fact, the additional load on evaporators would be approximately equal to the evaporation load added by a steffen house, and evaporators will stay clean due to absence of scale forming salts (removed by ion-exchange).

In discussing dilution, one point should be emphasized concerning the apparent dilution; that is, loss of brix, occasioned by removal of non-sugars by the resins. Consider a 13.0 brix, 83 purity diffusion juice, going through the exchanger with no dilution and with an effluent purity of 97.

100 lbs. of Raw Juice then contains

Solids	13 lbs.
Sugar	10.8
Non-Sugar Solids	2.2
Water	87.0
	100 lbs.

After passing through the exchanger:

Solids	11.1
Sugar	10.8
Non-Sugar Solids	0.3
Water	87.0
	98.1

The brix of the effluent juice will then be $\frac{11.1}{98.1}$ = 11.3. Thus, the brix decreases 1.7 without the addition of any water whatsoever.

Resin Losses and Regenerants. Measurements were made on the amount of resins lost during operations, and it was found that all the loss was mechanical; that is, loss of resin during back wash. No evidence of attrition or decomposition of resins was noted. For the entire campaign, the loss of cation resin (Ionac C-200) was 5 per cent. The anion resin (Ionac A-293-M), however, was much more inclined to carry over during back wash, and a loss of 26.5 per cent was experienced about half way through campaign. New resin was added to original level and steps taken to prevent loss in backwash. After this, no measurable loss was experienced. For estimating purposes, however, both anion and cation resin loss is calculated at 5 per cent per year.

One of the big problems of the pilot plant was, of course, to discover the minimum dosages of regenerants necessary for good operation since the economies of ion-exchange revolve largely about these quantities. A great deal of time was spent in determining these amounts which were found to be as follows:

100% Caustic	17 lbs. per ton beets
100% Acid	19 lbs. per ton beets