Recovery of Waste Ammonia in Ion Exchange Operation

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In the commercial application of ion exchange to the purification of beet sugar juices as practiced at the Hardin, Montana, plant, ammonia is used to regenerate the anion column. The amount of ammonia used per cycle ranges from 400 pounds to 600 pounds. Of this amount approximately 250 to 300 pounds is fresh make-up and the remainder is recycled regenerant. There are 412 cubic feet of Duolite A-2 resin in each anion column. The fresh ammonia requirements are approximately 5 to 7 pounds per ton of beets. This figure rises as the purity of the beets drops. Ammonia at Hardin
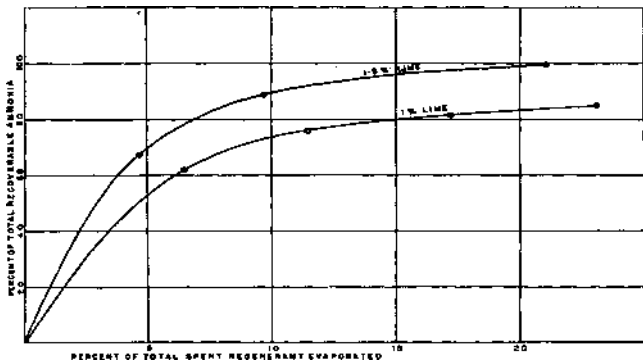

Figure 1.

is very expensive in part because of freight. A study was conducted there with the objective of reducing ammonia requirements in ion exchange by recovery of ammonia through distillation of spent anion regenerant.

In the present system of regeneration at Hardin, after backwashing, a solution of ammonia from 2 to 4% is passed through the column. The effluent from this column goes first to the spent regenerant tank. The flow continues until a large proportion of the impurities held by the anion column has been displaced. At this time the concentration of ammonia in the spent anion regenerant has become relatively high and the flow is diverted to the ammonia make-up tank. This provides a solution relatively rich in ammonia and fairly low in impurities into which is later added fresh

ammonia for regeneration of the next anion column. Once these require-
ments have been met the flow is again diverted to the spent anion tank.
The spent anion tank and the spent cation tank, which contains acid from
regenerating the cation column, are dumped simultaneously to the sewer
in order that much of the sulfuric acid in the spent cation regenerant can
be neutralized by the ammonia.

Preliminary studies were made to determine the approximate concentra-
tion and amount of ammonia which could be freed by distillation from the
spent anion regenerant. Several results were obtained:

**(1) A relatively small proportion of the total volume of spent anion
regenerant had to be distilled in order to free a large proportion
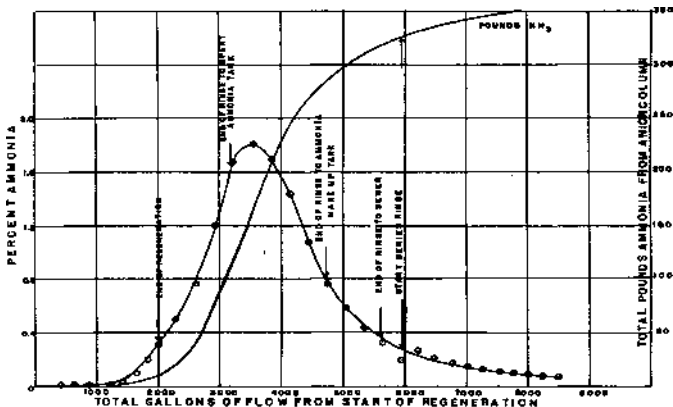of the distillable ammonia.**

Figure 2.

**(2) It was found that if one distilled ammonia from the spent anion
regenerant there would be frequently, but not always, a white
precipitate which would foul the surface of the condenser.**

**(3) It was next determined that the use of lime added to the spent
anion regenerant allowed one to recover more ammonia than if
no lime was added; it allowed one to recover ammonia at a faster
rate; it prevented the formation of the white scale on the ammonia
condenser.**

The amount of ammonia in the spent regenerant was found to vary
between 0.5 to 1.0% distillable ammonia. Figure 1 presents results for

experiments in which two levels of lime were added to the spent regenerant followed by distillation. It will be seen that if 1% lime is added to spent regenerant that by evaporating 10% of the total volume of liquid one can recover approximately 75% of the total distillable ammonia, and by distilling 20% of the total volume one can recover approximately 82% of the total distillable ammonia. When one adds 1.5% lime, he can recover 90% of the total distillable ammonia by distilling only 10% of the spent re-
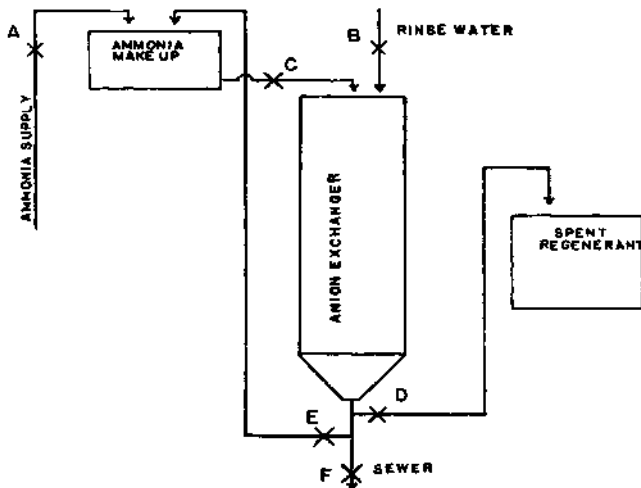
REGENERATION FLOW

Figure 3.

generant, and finally if one distills 15% of the total volume he can recover 97% of the total distillable ammonia when 1.5% lime is added. In order to obtain the last remaining 3% of the total distillable ammonia one would have to distill another 714% °f ᵗʰᵉ water. Not shown in Figure 1 are data obtained where 2% and 3% lime on spent regenerant were added. The curves were very slightly steeper at 5% evaporation but practically identical at 10 and 15% evaporation with the curve obtained with 1.5% lime. It was interesting to note that the condensate obtained by distillation of spent anion regenerant had almost exactly the right concentration of ammonia for regenerating the anion column. It should also be pointed out that the

results were substantially identical whether the distillation was carried out by heating the regenerant *in* a flask or by injecting live steam into the solution. The latter technique was studied because in commercial practice we would expect difficulty from scaling of heat transfer surfaces.

Figure 2 shows concentrations of distillable ammonia plotted against gallons of flow from the start of the regeneration cycle at the Hardin plant.
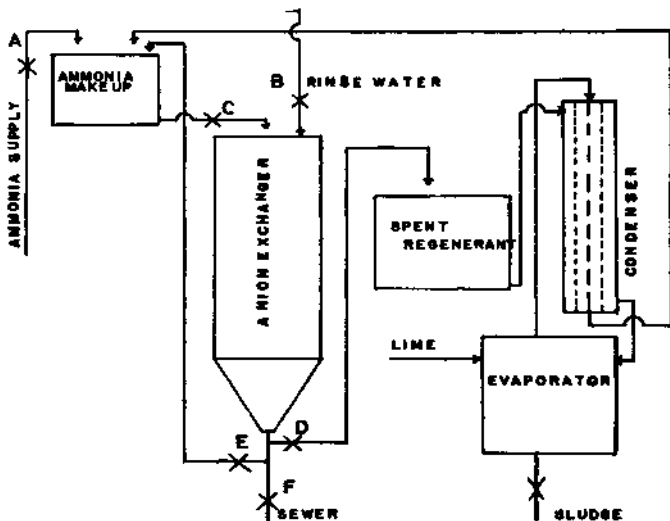
REGENERATION FLOW WITH AMMONIA RECOVERY

Figure 4.

The top curve shows the cumulative total pounds of ammonia from anion column from the start of the cycle. It shows the various operations in the regeneration cycle. From this graph one can determine what the amounts and concentrations of ammonia would be if one saved only spent regenerant having 0.2% ammonia or greater. This was done, neglecting that amount of ammonia which goes to the ammonia make-up tank since the present anion exchange system already reuses this ammonia profitably. This cut, between 3,240 and 4,740 gallons, is used to dissolve fresh ammonia for regeneration. In the first study made, it was found that 260 pounds of fresh

ammonia were used on each cycle and that one could recover by distillation 138 pounds of ammonia from a selected cut of the spent regenerant obtained by the flow volume 1,440 to 3,240 and 4,740 to 5,640. This represents a reduction of approximately 50% of the fresh make-up ammonia requirements. From Figure 2 it was calculated that the percentage ammonia should be 0.75%. A subsequent series of determinations gave a calculated average concentration of 0.81% recoverable ammonia for the same portions of the cycle. A large composite sample (45 gallons), representing these portions and made from several cycles, showed an actual concentration of 0.83% recoverable ammonia. The regenerant solution in these cases was stronger than had been used previously. The recovery would be effected by the use of 1.5% lime and 15% distillation. Economic analyses indicate that this would be a very profitable operation on a plant scale. One of the principal advantages of the system is simplicity. For example, in contrast to many ammonia recovery systems no complicated equipment, compressors, etc., are needed. One simply distills the ammonia, the vapors are condensed on a water cooled condenser and are reused. The water cooled condenser can operate as a preheater for the feed. Figures 3 and 4 show the old system of regeneration and the new system modified for recovery of ammonia. The process is covered by a patent application.

Ion Exchange Behavior on Two-Boiling System at Layton Sugar Company

DONALD M. STROMQUIST

The 1949 campaign at the Layton Sugar company was a short but successful campaign and its success was due in part to the method of operation and in part to the deionization equipment installed there in 1947 by the Illinois Water Treatment Co. This equipment consists of four pairs of ion-exchange units which are interconnected by a common system of four, five, and six-inch piping which conveys juice, water and regenerants in their proper order to the cation and anion cells. The cation cell is 10 feet by 14 feet and. holds approximately 625 cubic feet of cation resin; the anion cell is 10 feet by 11 feet and now holds approximately 412 cubic feet of anion resin. This resin balance permits treatment of 1,300 tons of beets per day with each unit operating on an average one and three-quarter hour cycle. The units treat cooled second carbonation beet juice and then pass the resultant deionized high purity juice back into the process at the evaporation station. Fluid flow is controlled manually by Hills-McCanna saunders patent valves. The regenerant tanks which are common to the four units have the proper amounts of chemicals metered into them by automatic controls. Bulk storage tanks for concentrated sulfuric acid, 20% caustic, and 20% ammonium hydroxide are provided. All tanks, as well as necessary piping, are rubber lined.

In a normal deionization operation on beet sugar juices such as the 1948 operation at Layton, the order of cycle is—backwash, regeneration, rinse, service, sweetening off and then a repetition. In 1947 and 1948, we treated the second carbonation juice *in* its entirety, and in instances experimentally returned various diluted greens without too much success because of excessive color build-up. Because of the resulting more intensely colored influent juice, the ion exchange units would operate at a lower efficiency and would slip color bodies back into the process. Thus it was evident that, in order to obtain ultimate extraction, some system of color removal from sugar juices was necessary. A multiple boiling system was not the answer either because repeated contact of the unbuffered juices with the heating surfaces intensifies the juice colors even more. This of course makes it increasingly difficult to obtain a third white sugar strike.

Table 1.—Regenerants Used **in 1948 and 1949 in Pounds per Ton of Beets.**

Regenerant	1948	1949
Sulfuric Acid	12.94	17.75
Ammonia	5.68	7.00
Caustic Soda	2.45	5.05
Cost per Ton of Beets	47.98¢	71.9¢

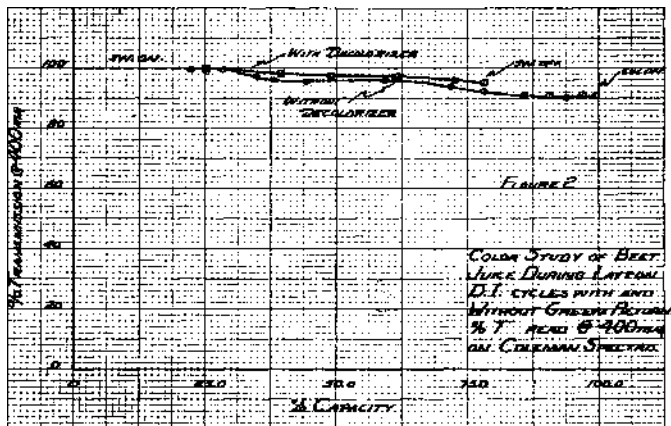[1] Research Chemical Engineer, Illinois Water Treatment Co.

Experiences during the inter campaign period in color removal from deionized molasses for the production of an edible syrup gave us the answer to the proper mode of operation. For the de-colorization we employed a regenerable granular phenolic resin that when properly applied was quite efficient in removing color bodies from sugar solutions. During campaign, this material was utilized in three 42-inch by 10-feet tanks which were designed similar to deionizer reactor tanks, and were handled in a like manner, i.e., one on stream while the others were being regenerated. The material from which we removed color bodies was the green syrup from
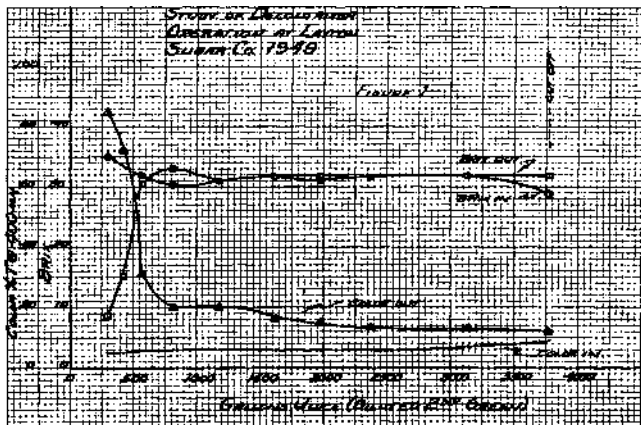
the second white pan. We obtained two white strikes of sugar from our deionized standard syrup and then decolorized the diluted second green by percolating it through the granular regenerated decolorizer. A dilute solution of caustic soda was used as the regenerant. After color removal, the green syrup was introduced into the process again at the beet end, where practically all invert was destroyed by means of carbonation. The brix of the material treated was cut from about 70 to 35 with thin juice, and each decolorizer unit performed for approximately six hours at flows ranging from 25 to 30 gallons per minute. By utilizing thin juice for the necessary reduction in brix, we avoided adding any excess water to the process other than the dilution inherent to sweetening on and off the decolorizer units. Color removal is actually greater than the 7 percent indicated at the end of the run because it is a log rather than linear relationship.

The second green syrup contains a concentration of all the solids which have once slipped by the ion exchangers plus an accumulation of color bodies and caramels which are the result of continued contact of a sugar bearing

solution with heating surfaces. The anions contained in this green return were experimentally determined by decationization of a 35 brix solution and were found to be in excess of 200 grains per gallon ($CaCO_3$ equivalent). Most of the acids thus determined titrated in the pH range of 3.5 to 4.0, proving that they were for the most part weak acids, which are very difficult to remove in any excess by means of a weak base anion exchanger such as that employed at Layton. A flow of 30 gallons per minute of such a green syrup is equivalent to at least 60 gallons per minute of thin juice, which would account for more than 15% of the capacity of each ion exchange

Figure 2

Color Study of Beet Juice During Layton D.I. Cycles with and Without Green Return. % T. Read @ 400 mµ on Coleman Spectro.

unit. By taking the nature of the acids into consideration, that is, their low dissociation, the return would take up 20% of the resin capacity and in particular the capacity of the anion exchanger.

Even though the individual beet juice cycle is shortened materially by green recirculation, very little difference is noticed in color removal from thin juice incidental to ion exchange because color concentration is of the same order as that in second carbonation juice without decolorized green. The fiinished juice in either case is colorless to the naked eye and proved of excellent quality when color readings were observed on a spectrophotometer. Similar readings were observed throughout the campaign and none was observed below 90% transmittance.

Of the two resins necessary for deionization, that is, cation and anion, it is evident that the cationic resin is quite stable and the anion resin is subject to deterioration if proper care of the resin is not observed, and particularly so in sugar work. In the deionization of beet sugar juices we

have many cycles per day, a wide variety of dissolved solids in the juice other than sugar and in general quite severe conditions not usually found in other applications. In spite of this, the cation resin at Layton has been used for three campaigns with little or no deterioration. The anion resin has been used for two admittedly short campaigns with quite favorable results. The exhaustant used was a mixture of mineral and organic acids, the concentration of which was 100 grains per gallons ($CaCO_7$ equivalent) and the nature of which simulates the beet juice treated. It is interesting to note the initial reduction in capacity experienced on the new resin and the leveling off or slow loss in capacity from that point on. The anion resin has retained its hard granular texture and is still light in color, both being physical indications of a minimum loss in capacity. As this particular anion becomes damaged, it first loses its ability to absorb weak organic acids and it seems to have lost little or none of its efficiency for this adsorption. The cation resin bed depth is substantially the same, but some anion resin has been lost due to its fine nature. In our opinion it would be wise to control grain size of this material to larger than 30 or 40 mesh to minimize loss from fine particle carry over in backwash.

This year's chemical cost figures are higher than those obtained on the 1948 operation. There are several factors which contributed to the increased cost and the higher chemical consumption. These figures include the chemicals used for the three decolorizer units, as well as the pilot ion-exchange syrup plant, both of which measurably increased the caustic and acid consumption. Then, too, recirculation increased our large deionizer regenerants by some 20% because of the resulting increased solids content of the thin juice. However, these increased costs are offset by a considerable margin, because by their use we obtain an overall extraction of 96.5%.

The deionization station operated exceptionally well during the 1949 campaign and gave no trouble other than minor mechanical difficulties. For the entire campaign we averaged fifteen regenerations a day, which gave us an average hour and 36 minute run and an ample four and three quarters hours regeneration time. In considering how many regenerations we should have obtained with a 20% overload, we may take 20% of the rated thirteen daily regenerations and add it thereto and come very close to the amount we actually obtained. No difficulty was experienced with maintaining pH in the evaporators. Standard juice samples read from 30 to 40 percent transmittance at 410 mu over the entire campaign—this particular color being a very light straw yellow. Dilution figures are not available for this year's run because on occasions we were forced to split our stream on sweetening off, i.e., we pushed some juice ahead to the evaporators and some back to the second carbonation bumper tank, because of limited effluent pump capacity. This of course made our meter readings somewhat ficticious.

We also noticed that the pH of the finished juice during the deionization cycle followed a normal pattern. The intial pH generally had a value of 9.0 to 9.5 and dropped in a sloping curve to a pH of 7.0. This is favorable in that it gives little or no evidence of oxidation of the reactive groupings of the anion resin.

At the conclusion of the 1949 campaign, practically all greens were

recirculated through the ion exchange plant in order to speed up the clean-up and also to get all available sugar into the bag for remelt the following year. This permits the retention of granulated sugar rather than lower purity syrups.

After the campaign, we started the processing of two tank cars of straight house molasses as an experiment in order to determine the feasibility of making white sugar out of such a material when it could be contracted at a good price. Some difficulty was had because the dilution control was poor but indications were that such an operation would be desirable. The material at 10 brix gave us a favorable cycle and also enough water to keep the evaporators from idling. We produced a near water-white juice after the dilution difficulty and managed to sack 575 bags of white sugar. The
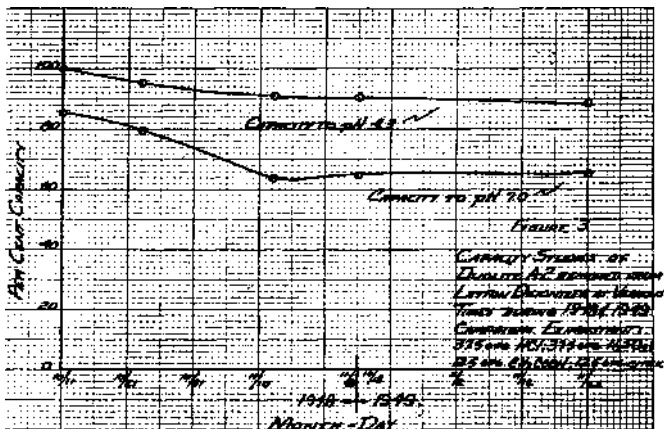
rest of the syrup and greens was set aside for brown sugar and edible syrup production. A continuous operation would naturally *give* us a better run than the short experimental run obtained in less than a day on 100 tons of molasses.

As more experience is gained on the deionization of beet sugar juices and sryups, it becomes more apparent that it is a useful tool, and well worthy of incorporation as a station *in* a beet house. Its many advantages, low molasses production, no rumbling or cleaning of heating surfaces, high purity juices, absorption of beet end fluctuations, etc., are dividends which cannot be ignored.