The Application And Utility Of Magnesium Exchange In The Beet Sugar Process

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Introduction and History

The highly melassigenic effect of the alkali salts was suspected as early as 1843 by Hochstetter (4)[2]. Thompson and Way demonstrated the ability of soils to exchange alkali ions for the divalent alkaline-earth metal ions before the turn of the century.

Ruembler (8) applied for a patent as early as 1869 and patents were issued to Harm in 1896 (3) and to Gans in 1905 (2).

Claassen (1), in 1907, was perhaps the first to show the true nature of increased extraction by reducing solubility of sucrose through removal of alkali ions in exchange for divalent alkaline-earth ions.

According to Quentin, (6,7) sucrose solubility in molasses increases with the presence of cations as shown in Table 1. The ion exchange process which removes alkali ions in exchange for magnesium ions via synthetic cation exchanger carries his name. Moebes (5) found similar values in an investigation carried out at about the same time.

Table 1.—Relative sucrose solubility in the presence of certain cations.

Mg^{++}	<	Ca^{++}	<	Li^{+}	<	Na^{+}	<	K^{+}
.61		.66		.73		.94		1.0

There are now some 50 Quentin plants in operation in Europe. Most are in West Germany, some are in Austria, Holland, France, Italy and Belgium. All are operating successfully and are much appreciated by the factory personnel.

Results and Discussion

Laboratory

Like others before us, the Research Department of the Amalgamated Sugar Company found a direct relationship between sucrose solubility in molasses and the concentration of alkali ions. Figure 1 illustrates this relationship.

An exchange of 50% of the combined potassium and sodium for magnesium via cation exchange resin brought a remarkable reduction in sucrose solubility as shown in Figure 2. Laboratory

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[2] Numbers in parentheses refer to literature cited.

boiling tests were carried out to explore boiling behavior, crystallization rates, crystal habits and purging qualities.

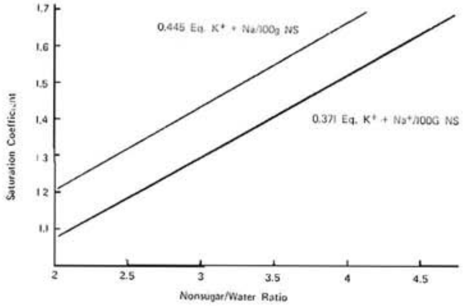

Figure 1.—The effect of potassium and sodium upon the solubility of sucrose in intermediate syrup. Coefficient of saturation vs. nonsugar/water ratio.

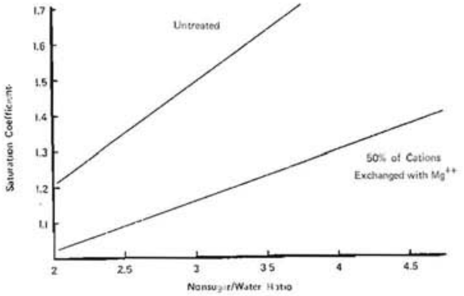

Figure 2.—Reduction of sucrose solubility through ion exchange of intermediate syrup. 50% exchange. Coefficient of saturation vs. nonsugar water ratio.

$$R-(SO_3-)_n^{=}-(Mg^{++})_{n^1}+K^+/Na^+ \rightleftharpoons R-(SO_3-)_n^{=}-K^+_{n^2}/Na^+_{n^3}+Mg^{++}_n$$

The information gathered indicated that boiling practices need not be significantly altered as long as the nonsugar water ratio remains below 2.0 where solubility differences are relatively small. This range covers the seeding and most of the feeding period. Factories which Brix up to a high nonsugar/water ratio will have to decrease the final temperatures by up to 10° C., depending upon the exchange rate, fillmass purity and vacuum used, respectively.

Molasses purities as low as 43% T P were obtained under conditions of high magnesium exchange (e.g. $> 60\%$) in the laboratory boiling tests. However, lumps were formed whenever syrup with a high exchange rate was used. The lumps were especially bad with one type of catex resin used. The application of an agitator in the laboratory pan, change to a different type of resin, and exchange rates below 55% eliminated all crystal fusing (lumps).

The purging quality of the magnesium fillmass was remarkable, allowing hot centrifuging immediately after pan drop, even with low purity (e.g. < 75% T P) fillmass.

It was not possible to build a reasonable grain with the same stock syrup, but prior to magnesium exchange and purities below 75% S.A.T.P. Likewise, the non-magnesium fillmass did not allow clean purging prior to a full crystallizer cycle even for fillmass purities around 78%.

Laboratory tests also established and confirmed earlier findings, that it was not practical to utilize the full potential of magnesium exchange by maintaining normal fillmass purities around 78 to 80%. As a rule of thumb, a 20-point purity spread between the fillmass and final molasses is about as good as can be expected. Mobility of the fillmass restricts further exhaustion via continued crystal growth even though average supersaturation and temperature may still be adequate for further growth. Lubrication between individual crystals becomes inadequate when the crystallized sugar in the fillmass represents more than 45% of the total mass. Thus, it is essential to reduce fillmass purities with magnesium exchange. This is a welcomed necessity for most operators since many factories have difficulties maintaining a 78 to 80% S.A.T.P. low raw fillmass purities without extensive spiking with high green.

Magnesium exchange via strong catex is a relatively simple procedure. Resin selection must be guided by requirements such as:

1. Superior physical strength to resist osmotic shock.
2. Excellent hydraulic characteristics to minimize pressure drop through the resin bed when using high Brix syrup.
3. Exchange selectivity profile allowing maximum utilization of exchange capacity during exhaustion, yet minimum regenerant demand during regeneration.
4. Resistance to fouling.

Our work in resin screening merely confirmed that others had done good work in this area, although we found that one particular resin which otherwise gave excellent results yielded a syrup which produced a lumpy fillmass in laboratory test.

The relationship between cumulative exchange rate for intermediate syrup in percent combined sodium and potassium exchanged for magnesium and the effective operating capacity of strong, macroporous cation exchanger operating over the magnesium form is illustrated in Figure 3. All values from six consecutive pilot plants run with an improved cell design are represented.

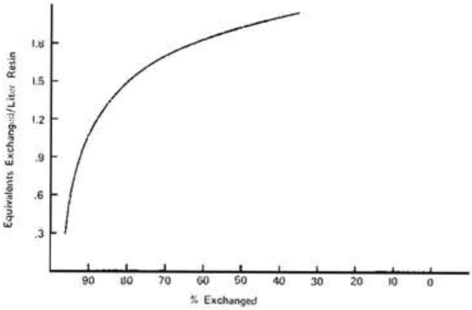

Figure 3.—Exchange rate vs. operating capacity of Nekrolith R. P. P. over the magnesium form when exhausted with intermediate green. (laboratory data.)

Figure 4 shows similar information for the commercial installation at Nyssa. Actual operating capacity is about 20% less due to the magnesium recycle load through low raw sugar and the normal calcium background concentration not deducted in Figure 4.

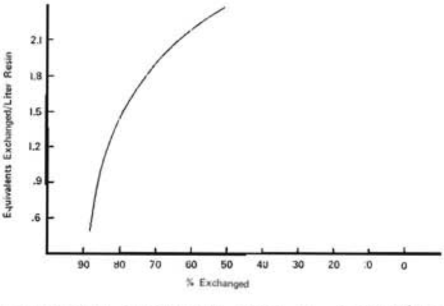

Figure 4.—Cumulative exchange rate vs. operating capacity of Nekrolith R.P.P. over the magnesium form when exhausted with intermediate green. Nyssa factory data includes recycle.

Under well-controlled operating conditions, an actual operating capacity of 1.7 equivalent/liter resin is common in conventional installations.

The regeneration profiles pertaining to the operating capacities as shown in Figure 3 are illustrated in Figure 5.

It appears possible to achieve nearly complete conversion of the exhausted cation exchange resin to the magnesium form with about 25% excess regenerant without recycling once-used brine.

A typical concentration profile for the regeneration effluent from the regenerations as shown in Figure 5 is represented in Figure 6.

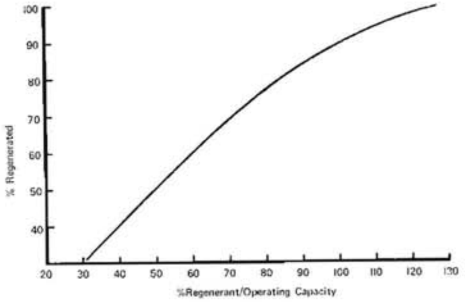

Figure 5.—Regeneration efficiency of Nekrolith R.P.P. when exhausted with intermediate green and regenerated with 1.4n MgCl, data from five laboratory runs with improved cell design.

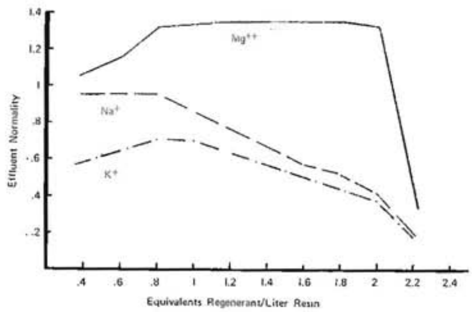

Figure 6.—Concentration profile of regeneration effluent from strong cation exchange resin exhausted with intermediate green and regenerated with 1.4 normal $MgCl_2$ solution. No recycle. Laboratory data.

Magnesium concentration increased rapidly after about 1.6 equivalents per liter resin had passed through the column. Thus, recycle of magnesium rich fractions beyond this point appears to be desirable for primary regeneration.

The concentration profile of the regeneration effluent with recycle of magnesium rich fractions is shown in Figure 7. It is evident that the recycled fractions promote better utilization of freshly-applied magnesium.

Under closely-controlled conditions it was possible to operate at only 10 to 15% excess regenerant on resin operating capacity when recycling magnesium rich fractions without a sacrifice in operating capacity.

Operating parameters were also developed for:

1. Factory most suitable for installation of such a unit.
2. Sequencing program and sizing of vessels, pipes and valves.
3. Anticipated pollution load.
4. Required and desirable instrumentation.
5. Extent of intended automation.

6. Cell design e.g. air dome vs. water dome.
7. Water demand and reuse of in-process water.
8. Optimum operating temperature profile for various process solutions.
9. Disposal of sweet water.
10. Optimum concentration of regenerant and acceptable brine quality.
11. Flow rates.
    a. Exhaustion
    b. Sweet-off
    c. Backwash
    d. Regeneration
    e. Regenerant rinse.

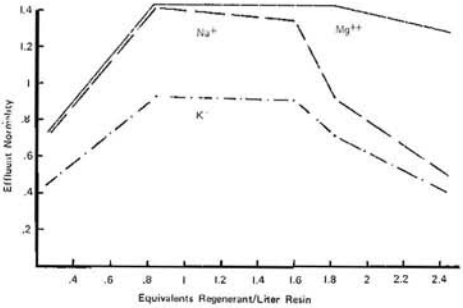

Figure 7.—Concentration profile of regeneration effluent from strong cation exchange resin exhausted with intermediate green and regenerated with 1.4 normal $MgCl_2$ solution. With recycle. Factory data.

Factory

The investigation clearly indicated that Mini-Cassia with its high potassium concentration of 0.365 gram equivalent per 100 grams nonsugars would be the most logical choice.

Nyssa factory, a Steffen house, was a close second choice. However, Mini-Cassia is a straight house and its molasses is used at the Twin Falls Steffen house. No information or experience was available on behavior of magnesium molasses in the Steffen house.

Thus, the risk of affecting the Twin Falls Steffen house operation negatively was the deciding factor in selecting Nyssa for the first installation.

The laboratory and pilot plant studies yielded information which allowed the preparation of a flow and timing schedule to illustrate the interrelationship of all process solutions at any time as shown in Figure 8.

Table 2 shows the sequencing program designed to allow maximum flexibility.

Table 2.—Sequencing program for Nyssa magnesium exchange.

Step	Identification	Solution in	Solution out	Termination of step
1	Sweet-on 1	Syrup	Rinse rec. water	Bx; timer; cond.
2	Sweet-on 2	Syrup	Conc. sweet water	Bx; timer; cond.
3	Exhaustion	Syrup	Syrup	Ion selective electrode: Timer; conductivity
4	Sweet-off	Conc. sweet water	Syrup	Tank level
5	Sweet-off 2	Diluted sweet water	Syrup	Bx; tank level
6	Sweet-off 3	Diluted sweet water	Conc. sweet water	Bx; tank level
7	Sweet-off 4	Condensate	Diluted sweet water	Bx
8	Backwash	Rinse recovery water	Waste	Timer
9	Resin settle			Timer
10	Regeneration 1	Once used regen.	Rinse recov.	Conductivity
11	Regeneration 2	Once used regen.	Waste	Tank level
12	Regeneration 3	Fresh regenerant	Waste	Timer; ion selective electrode; tank level
13	Regeneration 4	Fresh regenerant	Once use regen.	Tank level
14	Rinse 1	Condensate	Once used regen.	Conductivity; ion selective electrode
15	Rinse 2	Condensate	Rinse recov.	Conductivity
16	Backwash	Rinse recovery	Waste	Timer
17	Stand by			

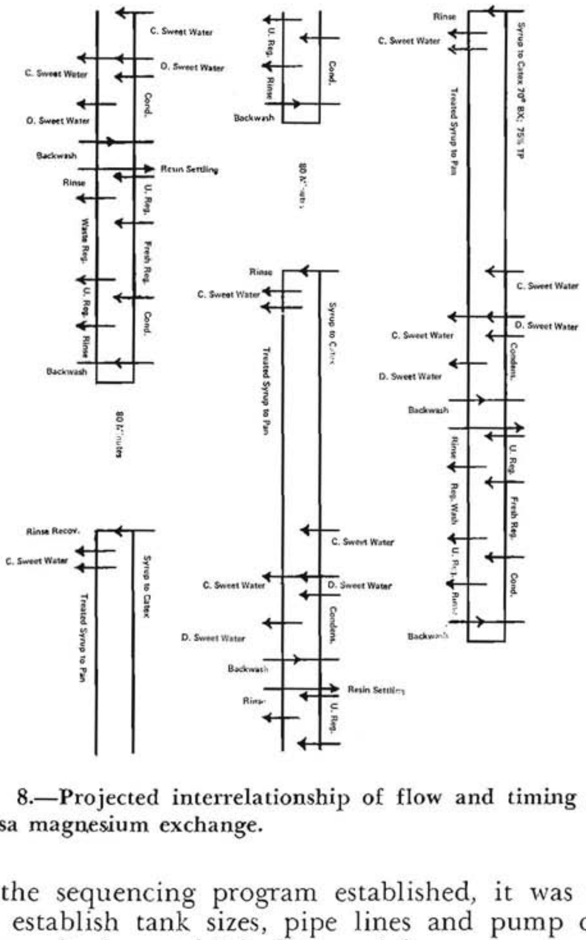

Figure 8.—Projected interrelationship of flow and timing sequencing for the Nyssa magnesium exchange.

With the sequencing program established, it was relatively simple to establish tank sizes, pipe lines and pump capacities. Furthermore, it also established the valving arrangement in the manifold header. Other design guidelines are shown in Table 3.

Fractionated sweetening-on and sweetening-off was planned, producing a concentrated sweet water of about 25 to 30° Brix and a diluted sweet water with a brix of about 5 to 10° Brix averagely. The diluted sweet water was to be used to dilute the untreated syrup to 70° Brix. Provisions were also made to use this diluted sweet water for washing the intermediate and low raw sugar, respectively.

The concentrated sweet water was scheduled to displace the syrup from the resin bed after exhaustion. Any leftover dilute sweet water was to displace the concentrated sweet water and condensate was to be use to displace the diluted sweet water in its respective sequence.

Table 3.—Guidelines for the design of a magnesium exchange plant at Nyssa.

7,000 tons beets sliced/day
2% nonsugars/beets
75% true purity of syrup to treatment
70 RDS of syrup to treatment
0.4 equivalents $K^+ + Na^+$ /100g nonsugars in syrup
50% of $K^+ + Na^+$ to be exchanged
177 equivalent to be exchanged/min.
120 GPM syrup flow
200 minute minimum reserve time
1.7 equivalent operating capacity/liter catex
2. Bedvol./hour (desirable flowrate)
500 cu. ft. catex/cell
135 minutes on stream
3 cells to be provided
5.5 feet maximum desirable resin height
11 feet diameter of cell
270 minutes reserve time available

Fresh regenerant concentration was to be 1.2 normal. Regeneration with freshly-prepared brine to be preceded by application of once-used regenerant which contained all fractions between 0.3_n during Mg^{++} breakthrough and 0.1 normal in Mg^{++} during regeneration rinse with an average concentration of about 0.6 normal.

All displacement waters and rinse waters below about 20,000 μmhos were to be recovered to be used for backwashing and brine dilution.

Condensate was to be used for sweetening-off, brine rinse, and make-up if required for rinse recovery.

Prior experience at Amalgamated with air dome operated ion erchange cells left some rather unpleasant memories. So we decided in favor of a water dome. A distributor system was selected which promised to give an undisturbed interface.

It was also decided to have fully automatic operation, but with manual override in all phases of operation. Thus, the following instrumentation for control purposes to maintain optimum operating conditions and correct sequencing would be involved:

1. Temperature; indication; recording; and control.
2. Pressure; indications only.
3. Flow; indication; recording; and control.
4. Storage tank level; indication; and alarms.
5. Conductivity; recording; and alarms.
6. Timers; alarms.
7. Brix, indication; recording; alarms; and control.
8. Specific ion electrodes; indication; recording; and alarms.

Engineering of the plant began about April 1, 1966 with actual operation commencing on November 14 of that year, five weeks after campaign began.

Operation continued uninterrupted to the end of campaign although the operation was not without problems.

Brix reduction during sweet-off proceeded rather fast, testifying in behalf of an excellent upper distribution system, but tailing in the low Brix region was abnormally long. Some of these tailings were traced to a high feed Brix during exhaustion (e.g. 80° RDS). In this case the diffusion rate lagged behind the displacement rate. Under these conditions sugar from the interior of the resin bead was released as late as during the regeneration step.

It is also extremely important to avoid an intermediate syrup Brix above 70° Brix for reasons of osmotic shock causing resin destruction and excessive pressure drop through the resin bed with its associated problems.

However, excessive tailing during sweet-off was also evident when feed Brix syrup was well controlled. A perfect interface between the water dome and the underlaid process solution as viewed through the sight glass gave evidence of excellent distribution from the upper distribution. A comparison of effluent Brix between internal rim and radial underdrain system and a sample line from the bottom of the cell indicated a puddle of heavy syrup remaining in the bumped head.

Figure 9 shows this comparison. Conversion to an underdrain system with external hub and internal radials improved the performance relative to dilution.

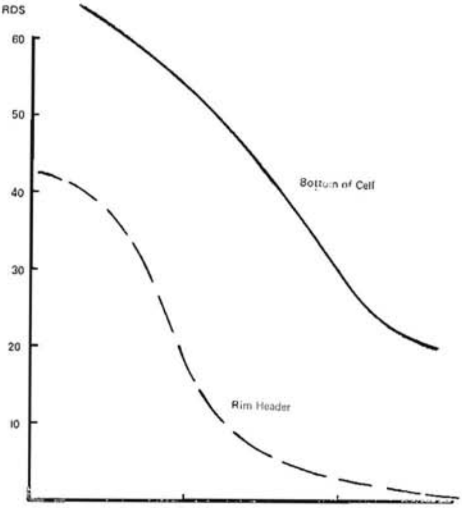

Figure 9.—Efficiency of rim and radial design underdrain during displacement of heavy Brix syrup with water.

A shutdown of the Mini-Cassia magnesium exchange was forced during the 1967 campaign when intermediate syrup pH was allowed to climb beyond pH 9.

Precipitation of $Mg(OH)_2$ occurred until operating capacity of the resin was reduced by 80%. Only an extensive acid treatment to dissolve precipitated $Mg(OH)_2$, followed by a caustic stripping to remove organic foulants restored normal operating capacities. Care must be taken to rinse the resin free of any caustic prior to its conversion to the magnesium form.

The results for the first year of operation at Nyssa are summarized in Table 4 and Figure 10 respectively. The primary operating cost for magnesium exchange in intermediate syrup is the regenerant.

Table 4.—Magnesium balance at Nyssa factory 1966 campaign.

4,184	tons	28% $MgCl_2$ to Process
10,462	tons	Nonsugars in Molasses
0.182	eq.	Mg^{++}/100 g Mol. N.S.
907.5	tons	Eq. $MgCl_2$ in Molasses Produced
3,239	tons	28% $MgCl_2$ in Molasses Produced
129	%	Regenerant/Operating Capacity
0.4	eq.	$K^+ + Na^+$/100 g Thick Juice N.S.
45.5	%	Exchange Rate

Table 4 shows a magnesium balance for the 1966 campaign at the Nyssa factory.

Brine consumption can be substantially reduced from the values indicated. Problems with the underdrain, inadequate backwashing, fouling of the resin when operating with high pH intermediate green, inadequate Brix control and fouling

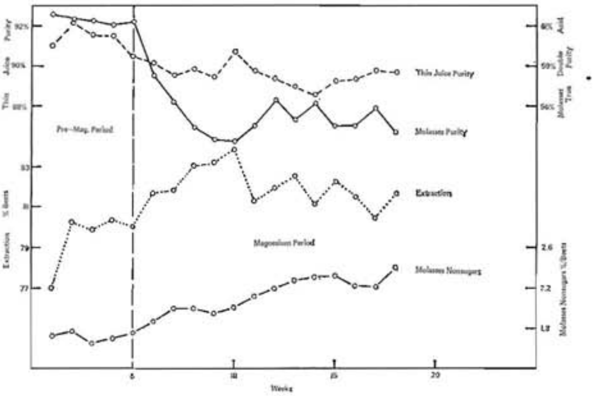

Figure 10.—Interrelationship of nonsugar load, molasses purity and extraction before and during magnesium exchange of intermediate green. Nyssa factory 1966/67.

of the resin with iron and defoamer additives all led to a waste of operating capacity and regenerant, respectively.

Figure 10 relates the critical data which influenced extraction for the 1966 Nyssa campaign.

A declining extraction beyond the 10th week is normal with advancing campaign.

The increasing load of nonsugars not removable in conventional juice purification forces a progressive reduction of thin juice purity and thus in extraction, when operating with stored beets.

Peak thin juice purity was already reached during the second week.

The progressive increase of molasses nonsugars clearly reflects this trend. Average extraction for the magnesium period is handicapped by this trend when compared with the average pre-magnesium period. Peak extraction was obtained in the tenth campaign week with about 4.5% over the average extraction of the pre-magnesium period (first week not included). This peak coincided with the lowest molasses purity while thin juice purity was still about 0.5 points lower than the average pre-magnesium period.

Molasses composites were prepared representing molasses production for three weeks prior to the magnesium period and three weeks after magnesium exchange start-up, respectively. These composites were analyzed in duplicate at our research laboratory according to the single acid true purity, double acid true purity and by the Spreckels Sugar Company by the isotope dilution method. The values are shown in Table 5.

Table 5.—Molasses purities before and during magnesium exchange.

	Before I.E.	During I.E.
SATP	59.20	53.50
DATP	61.56	55.31
IDTP	62.95	56.71

Respective campaign averages are shown in Table 6.

Table 6.—Molasses purities during the 1966-67 campaign. Nyssa Factor, Respective averages.

	Before I.E.	During I.E.
SATP	59.1	52.89
DATP	61.01	56.29

On the basis of the respective 1966 campaign average and the isotope dilution true purity method for molasses, the increased extraction due to magnesium exchange amounted to 0.52% on beets.

The results at Nyssa prompted the installation of a magnesium installation at Mini-Cassia factory, operative during the 1967 campaign.

A test run with Nyssa magnesium molasses at the Twin Falls Steffen house established the operating parameters for these conditions. It was discovered that magnesium molasses imparts superior operation to the Steffen house performance by reducing filtration rates to about 50% of the normal filtration rate. The improved Steffen house performance allows an increased capacity of 15 to 20% on sugar entering the Steffen house. However, increased cake thickness is often associated with inferior cake washing. This, together with the low purity of magnesium molasses, results in a reduced saccharate cake purity, and thus a larger nonsugar load from the Steffen house to carbonation. A deterioration of the settling rate and filtration rate at the first carbonation station was noticed together with an increase in thin juice lime-salts. These problems were easily mastered through minor adjustments at that station.

The well-proven Nyssa design concept was applied at Mini-Cassia with a few minor modifications in certain control loops. Performance at Mini-Cassia was similar to that observed at Nyssa.

A comprehensive trial was carried out during the 1968 campaign to evaluate magnesium exchange and its relationship in the entire economic structure of the company. For this purpose magnesium exchange was discontinued for a period of time toward the end of campaign at Mini-Cassia as well as at Nyssa. Non-magnesium molasses produced during this period was shipped to Twin Falls to be compared against the now normal magnesium molasses used in the Steffen house.

Mini-Cassia magnesium molasses was also shipped to Nyssa for a comparison in the Steffen house with the normally used non-magnesium molasses. Some results are shown in Table 7.

Table 7.—The economical interrelationship of magnesium exchange in intermediate syrup.

	Additional extraction % on beets
Mini-Cassia Mag. Exchange + Twin Falls Non-Mag.-Mol. (in the Steffen house)	0.657
Mini-Cassia Mag.-Exchange + Twin Falls Mag.-Mol. (in the Steffen house)	0.674

Although magnesium molasses yields a lower sugar recovery through the Steffen house (approximately 84 lbs less sugar recovered per ton of molasses at Twin Falls), the higher Steffen house capacity (average increase 14%) more than offset the decrease in sugar recovered per ton of molasses worked.

The values in Table 7 are considered high and may also reflect operational shortcomings when discontinuing magnesium exchange.

Magnesium exchange in intermediate green relieves the low raw end by returning some reserves to an otherwise overburdened station. A station thusly overcrowded may not perform at optimum when deprived of the relief available through magnesium exchange.

In conclusion, it can be stated that magnesium exchange of intermediate green can make significant economical contribution to the processing of sugarbeets.

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