

A SUMMARIZED REVIEW OF PROCEDURES FOR THE OPTIMIZATION OF PRE-LIMING

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Introduction:

With respect to conventional, classical, juice purification systems, the optimization of the pre-liming step and the maximum precipitation of certain impurities in pre-liming is essential to the maximum overall efficiency of juice purification, satisfactory 1st carb underflow filtration characteristics and the highest overall non-sugar elimination from the raw juice being processed.

Deterioration in beet quality as a result of storage time and/or storage conditions, primarily related to changes in the alkalinity and buffering capacity of the raw juice, results in variation of the ideal parameters for optimal pre-liming performance¹. These changes in juice quality require correction in the adjustment of the related pH/alkalinity operating parameters. Furthermore, as raw juice throughput varies due to a change in raw juice flow rate, the ideal temperature for pre-liming along with the back-mixing characteristics of the pre-liming equipment are affected due to the resulting change in juice residence time and the dynamic performance of the equipment. Even if temperature adjustment is possible, other compensating measures relative to pre-limer pH profile and/or final pre-liming pH/alkalinity are likely to also be required.

The purpose herein is to summarize a stepwise procedure for optimizing the coagulation and precipitation of insoluble non-sugar constituents in the beet raw juice during pre-liming. This is essentially a three-step process that requires each step to be optimized and maintained at near optimum conditions to facilitate the optimization of the related, subsequent step(s). The three general steps for optimization are as follows:

1. Setting of the proper temperature of raw juice for the residence time in pre-liming equipment.
2. Establishing of the correct pH/alkalinity profile for the current throughput rate and juice quality.
3. Determination and control of the optimum pre-liming end point pH/alkalinity for maximum coagulation and precipitation of insoluble non-sugar components, primarily pectin.

The end result of optimal pre-liming conditions is the maximum coagulation and precipitation of certain non-sugar constituents. Among these are oxalate, citrate, sulfate, phosphate, protein and pectin substances. As shown in Figure 1, these substances are coagulated and precipitated at different pH/alkalinity points in the pre-liming process and, especially in the case of pectin, are driven to completion by the optimum final pre-liming pH/alkalinity.

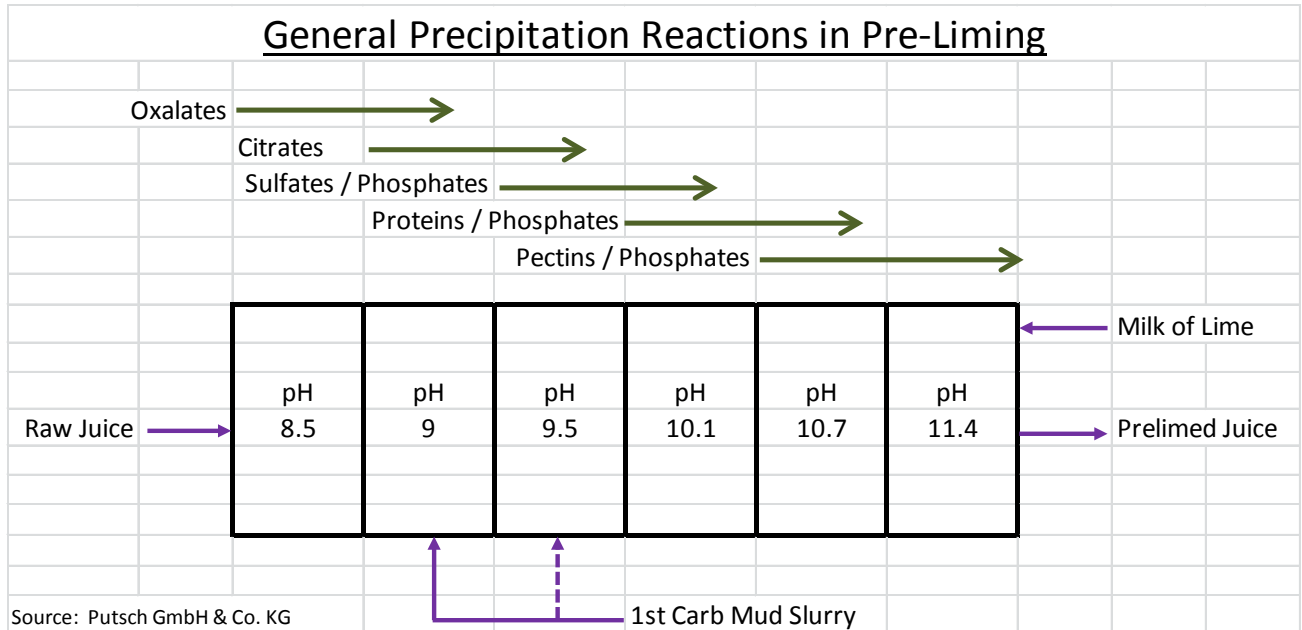


Figure 1

When the conditions of pre-liming are optimized, the pre-limed juice exiting the pre-limer will flocculate and settle quite rapidly leaving a very clear supernatant very similar in appearance to clarified 1st Carbonation juice. In fact, the filtered alkalinity of optimally pre-limed juice may generally also be regarded as the optimum target for the final, filtered 1st Carbonation alkalinity.

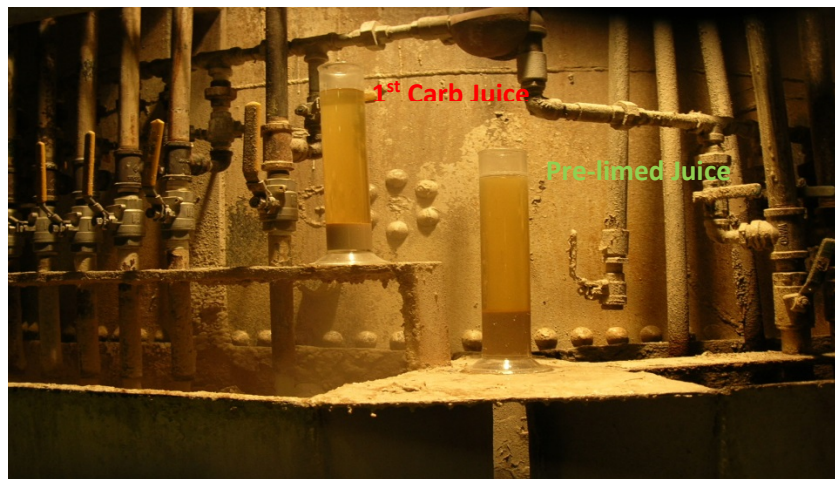


Figure 2

Establishing the ideal temperature / residence time relationship:

In existing factories employing pre-liming, the volume of the pre-limer is usually fixed, and thus the retention time in pre-liming is largely determined by the throughput of raw juice to the pre-limer. It is important to overall optimization that the flow and temperature of the raw juice as well as any sludge recycle and milk-of-lime be as stable as possible. In any case, only raw juice at the correct temperature, recycled thickened sludge at a relatively constant concentration and milk-of-lime at constant CaO concentration should be directed to the pre-limer. From a control perspective, the recycled 1st carbonation sludge and MOL may be ratio controlled to the pre-limer on the basis of raw juice flow. All recycle streams such as filter sluice, sump return to process, sweet-water, etc. should be directed downstream of pre-liming to insure steady-state operating flow and conditions to achieve optimum pre-liming process control.

Considerable work has been done by many investigators including Spengler et al. 1933, Madsen and Nielson 1978, Madsen 1988, Faviell et al. 1991, Kraus et al. 1997 on the subject of pre-liming temperature versus retention time with respect to optimization of coagulation and precipitation and resulting juice quality. Effectively, lower pre-liming temperature results in lower juice color, lower lime salts and increased purity of the purified juice. Table 1 indicates the expected effect of temperature on certain juice quality parameters.

Temperature °C	Raw Jc Effective Alkalinity g CaO/100ml	Thin Jc Color IU ₅₀₀	Thin Jc Lime Salts g CaO/100ml	Nonsugar Elimination %
20	0	311	0.109	25.7
30	-0.001	339	0.112	24.7
40	-0.002	395	0.129	24.6
50	-0.003	403	0.135	22.4
60	-0.005	405	0.158	21.7
70	-0.009	459	0.173	20.2
80	-0.013	549	0.2	18.6

Table 1
Influence of Pre-liming Temperature on Thin Juice Quality¹

The temperature at which pre-liming is carried out affects the optimum final alkalinity of pre-liming. Effectively, the higher the temperature of pre-liming, the lower the final end point alkalinity and vice-versa. The magnitude of this effect is 0.2-0.3 pH units lower when operating at a temperature of 40^oC versus 80^oC.

It is noted, where cold main-liming is employed after pre-liming, that colder pre-liming temperature (<40^oC) and shorter retention time is possible due to the fact that coagulation of pectin will continue in cold main-liming with alkalinity below 0.50 g CaO/100 ml.

In any case, if there is a change in pre-liming residence time and there is no opportunity for the adjustment of raw juice temperature, it is necessary to modify some of the pre-liming operating

parameters such as baffle positions to maintain a correct pH/alkalinity profile in order to maintain optimal coagulation and precipitation of the various non-sugar species. An alternative may be to adjust the operating juice level in the pre-limer to effectively adjust the retention time. If level adjustment is possible, it may also be necessary to make baffle adjustments in order to maintain the correct pH profile in the pre-limer. An adjustable weir at the pre-limer exit is ideal for this.

Figure 3 shows the literature reported “ideal” temperature to residence time range for pre-liming operations. The “standard” operating times relative to operating temperature may be calculated using the following formulas:

$$U_{\max} = (87.73 - 0.909 * t) + (6.694 - (80 - t) * 0.0761)$$

$$U_{\min} = (87.73 - 0.909 * t) - (7.999 + (80 - t) * 0.0909)$$

$$T_{\max/\min} = (96.50 - 1.10 * U) \pm ((55 - U)/10 + 4)$$

U = Residence Time, minutes

t = Temperature, °C

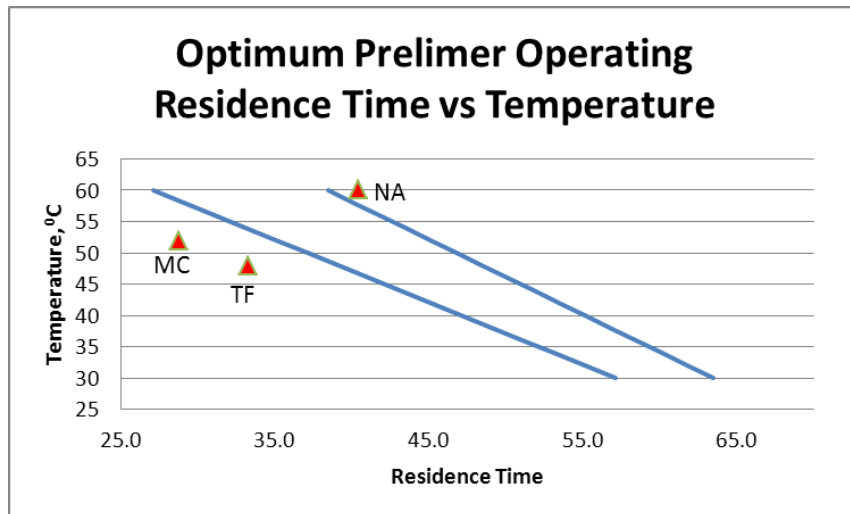


Figure 3

Low pre-liming temperatures may not result in complete pectin precipitation without being followed by cold main liming at < 0.50 g CaO / 100 ml. While MC and TF factories noted in Figure 3 exhibit lower than optimum pre-limer retention time, they are both followed by cold main liming thus negating the shorter pre-limer retention time. NA factory on the other hand has excess pre-limer residence time and is also followed by cold main liming. As a result, optimum pre-limer operating parameters at this factory are different than those at the other two factories.

The pH/alkalinity in cell #1 of the pre-limer should be held at a higher value when low pre-liming temperatures (< 45⁰C) are employed. Values in the range of 8.6-9.0 pH (0.015-0.020 alkalinity) will generally prevent undesirable microbial action.

Step 2: Establishing the ideal pH (alkalinity) profile

Once raw juice flow is stabilized and sludge recycle and MOL flow has been established and final pre-limer alkalinity in the approximately correct range, baffle adjustment may be made to obtain an ideal pH/alkalinity profile across the 6 cells of the pre-limer. Normally, the difference in pH in the first few cells will be smaller than the difference between the latter few cells. This will result in a more or less ideal concave pH curve across the pre-limer. When alkalinity is plotted across the six cells, the curve will appear to be far more concave than the similar pH curve.

The pH profile should be such that cell #1 is between 8.0-9.0 pH (0.005-0.020 alkalinity) with a normally ideal pH of about 8.5 (0.010 alkalinity). The final cell #6 pH/alkalinity should be at the optimum pH/alkalinity determined by the procedure for determination of the optimum coagulation end point pH described in the next section. Figure 4 shows the ideal profile for pH and alkalinity for a typical pre-limer operating at 50⁰C and a retention time of 36 to 46 minutes while Table 2 shows the numeric values for pH and alkalinity used in the graphs. Please note that the alkalinity measurements shown in the table are “filtered” rather than “whole juice” measurements.

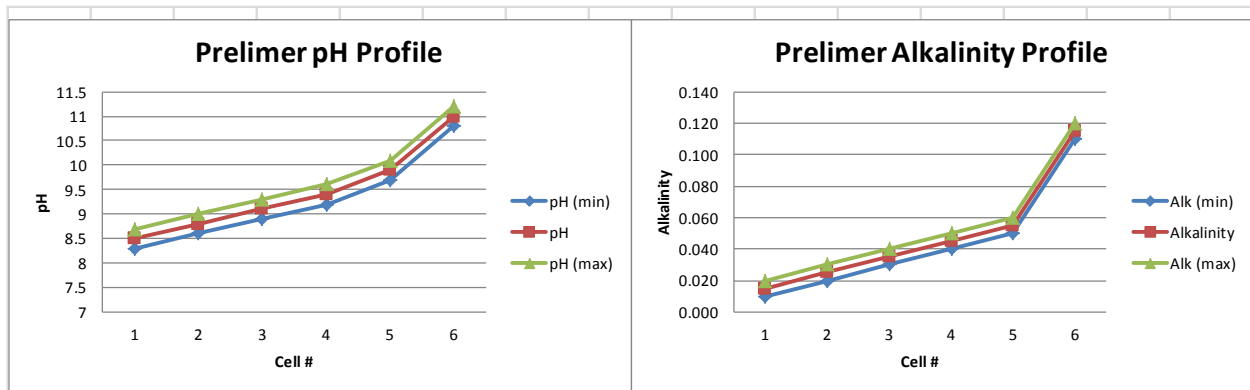


Figure 4

Ideal pH and Alkalinity Profile for Preliming						
pH (min)	pH	pH (max)		Alk (min)	Alkalinity	Alk (max)
8.3	8.5	8.7		0.010	0.015	0.020
8.6	8.8	9		0.020	0.025	0.030
8.9	9.1	9.3		0.030	0.035	0.040
9.2	9.4	9.6		0.040	0.045	0.050
9.7	9.9	10.1		0.050	0.055	0.060
10.8	11	11.2		0.110	0.115	0.120

Table 2

Baffle adjustment is generally necessary to maintain the ideal pH/alkalinity profile when there is a change in the raw juice flow rate to the pre-limer. Baffle adjustments are also usually necessary when there is a shift in the final pH/alkalinity to maintain optimum coagulation / precipitation performance relative to the optimum end point pH/alkalinity. The optimum final cell pH/alkalinity should be established at the beginning of campaign and as often as necessary as beet quality and the alkalinity (acidity) of the raw juice changes during the course of the campaign.

Step 3: Determination and Management of Optimum End Point pH (alkalinity)

The relatively precise determination and control of pre-liming final pH (alkalinity) is required in order to achieve maximum elimination of pectin/protein in juice purification. If complete coagulation of the insoluble non-sugars is not achieved in pre-liming, those impurities will remain in the juice resulting in reduced quality of juice produced from purification and potential issues related to 1st Carbonation mud and thin juice filtration.

The optimum end-point pH (alkalinity) of pre-liming is affected by the quality of the raw juice. The greatest influence is the alkalinity or buffering capacity of the raw juice. The optimum end-point generally shifts to higher values as the natural alkalinity of the raw juice increases which, in turn, also requires a higher lime addition to reach the optimum end point. Conversely, as the lactic acid concentration (or total acid concentration) of the raw juice increases, as with longer storage time or frost damaged beet, the optimum end-point pH (alkalinity) is shifted downward. The so-called “normal” range to be expected is approximately 10.6-11.6 pH.¹

During the course of the campaign, the optimum alkalinity will change as the quality of the beet being processed changes due to storage length or conditions. It is also likely, that fresh beet operations will have a different end-point from that of stored beet operations. Thus, it is important to determine the optimum end point experimentally at the beginning of each campaign and at suitable intervals (approximately monthly) during the beet processing period or whenever there is a substantial change in beet quality.

To the maximum extent possible, the optimum final end point pH should be controlled as precisely as possible to the experimentally determined optimum. To this end, it may be advisable to employ pH/alkalinity measurement and, perhaps even, automatic control of the MOL addition to the final cell of the pre-limer with the target set-point at the experimentally determined optimum value.

A detailed procedure for the determination of the final pH for optimum coagulation is attached as Appendix 1. This method of determination will give a relatively precise end point value and is the preferred method of analysis. A second, somewhat simpler procedure attached as Appendix 2, while somewhat less precise, is a “quick and dirty” method for getting into the correct range without using the more refined methodology described in Appendix 1. This method will give an approximate pH (alkalinity) range within which the operation should be controlled but will not

give the ideal target optimum pH (alkalinity). For precise control of the final pre-limer pH, the procedure in Appendix 1 is preferred.

General Operational Considerations:

Please make special note of the fact that to some extent, the optimization of each step of this procedure is interdependent on the other steps. However, there are certain operational guidelines in the adjustment of each step that must be followed. These guidelines are as follows:

- **ONLY** the final cell pH (alkalinity) is to be adjusted with **MOL addition** to the pre-limer.
- **ONLY** the individual Cell #1 through cell #5 pH (alkalinity) is to be adjusted by individual **baffle adjustment**. Such adjustments should be made when and only when the raw juice flow and recycle sludge flows are stable and at steady state flow rates and the final pH (alkalinity) is at the optimum.
- It is highly recommended that a cell sampling system be installed on the pre-limer in order to standardize the sampling of each cell. This is necessary for routine repeatable sampling of the system to achieve consistently relative results due to unavoidable sampling bias relative to the location that each successive sample is taken. Even the same operator cannot consistently sample the pre-limer in the absence of such a system since he cannot precisely duplicate the exact sample point on successive samples from the same cell.

Effect of Raw Juice Flow Variation on pH Profile:

Due to the normally fixed volume nature of pre-limer construction, any variation in raw juice flow will cause a departure from optimal pre-limer adjustment relative to pH profile and the desired processing temperature/retention time relationship. Such flow variation may especially be a problem when processing deteriorated or damaged beets at the end of the campaign but can be a problem anytime there is a change in Raw Juice flow rate.

Figure 5 shows the results of hourly pre-limer cell pH sampling during a period of somewhat erratic Raw Juice flow. During this 48 hour period, the operator continued to maintain a constant final alkalinity in cell 6. As noted in the cell pH data output, cell 1 pH showed the greatest variation relative to Raw Juice flow changes with decreasing degree of variation in subsequent cells. The variation in cell 1 was from 7.3 to 9.2 pH and in cell 2 from 8.1 to 9.5 pH. Optimum pH range for cell 1 is about 8.3-8.7 and about 8.6-9.0 for cell 2. Such flow excursions and resulting pH variation would at least affect the precipitation efficiency in these two cells for oxalates and citrates. Larger variation in raw juice flow would likely affect the higher number cells as well and a complete stoppage of raw juice flow, for even short periods of time, will result in an overall flattening of the pH profile in a relatively short period of time even if MOL addition to the pre-limer is also stopped.

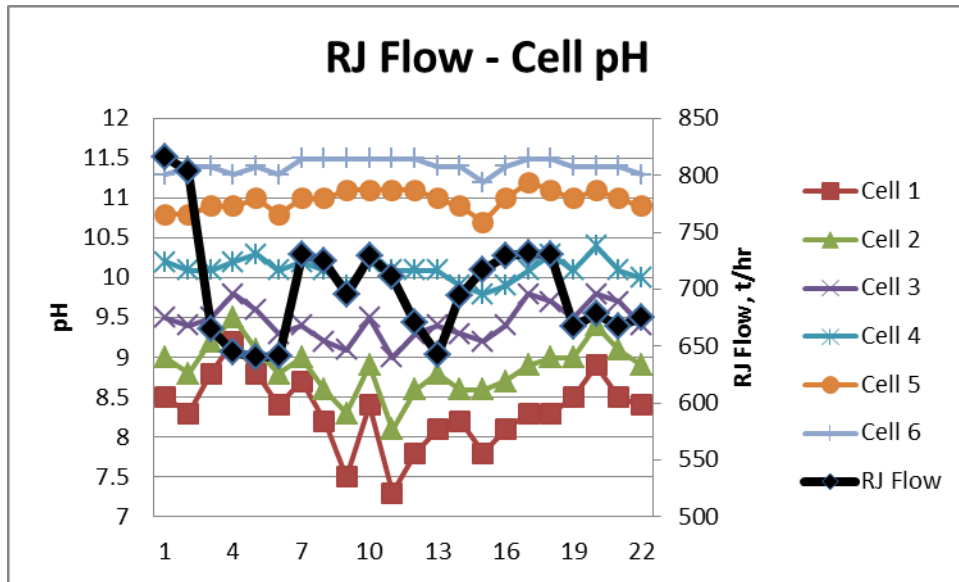


Figure 5

To prevent such pH excursions, a relatively simple control loop may be installed consisting of a pH meter to measure cell 1 pH and a VFD on the agitator drive. A set point is set for the cell 1 pH and a lower limit is set for the agitator drive speed to limit the range of speed reduction in the agitator. Such a system was installed and tested at the Mini Cassia factory of the Amalgamated Sugar Company, LLC in Paul, Idaho during the CY 2013 campaign. The resulting stabilization of the pre-limer pH profile is shown in Figure 6.

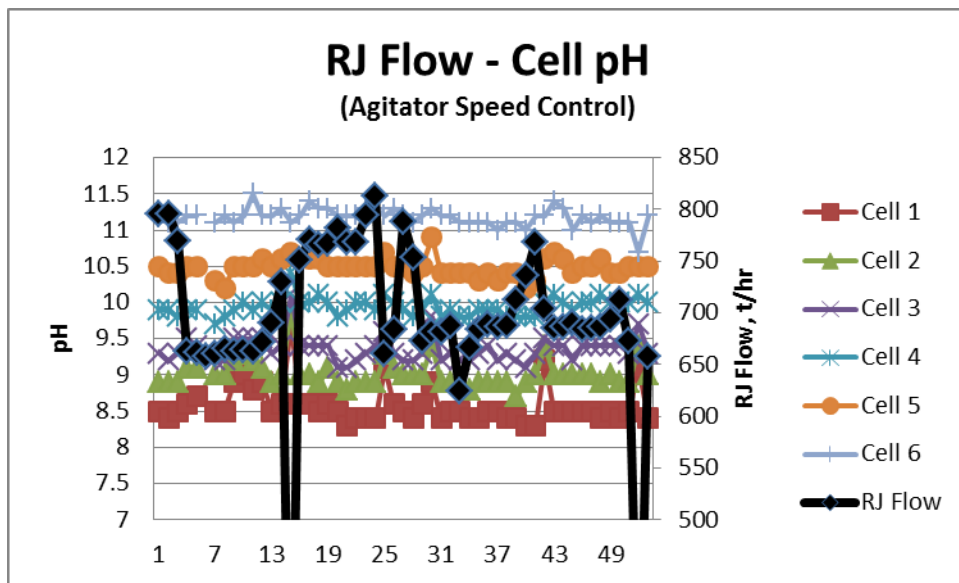


Figure 6

From a processing standpoint, the installation was made in an effort to stabilize pre-limer pH control and help improve 1st carb mud filtration characteristics during a period of particularly

variable beet quality during the final month of the campaign. The stabilization of the pH profile in the pre-limer clearly improved the 1st carb mud filtration performance during this period.

Variation in Optimum Final Pre-Liming pH:

As stated earlier, to assure relatively complete precipitation of impurities in pre-liming, it is necessary to establish the optimum end point pH/alkalinity and operate the pre-limer as close to the determined optimum as possible. Such determinations were made on an approximate monthly basis for the CY 2013 campaign at the Mini-Cassia Factory with the process optimized to these values to the extent possible relative to normal process variation.

During the early campaign prior to January 1st, the evaluation of optimum end point gave relatively consistent results with the factory operating at or very near the determined optimum with excellent purification non-sugar elimination and 1st carb mud filtration characteristics. The values of these determinations are shown in Figure 7.

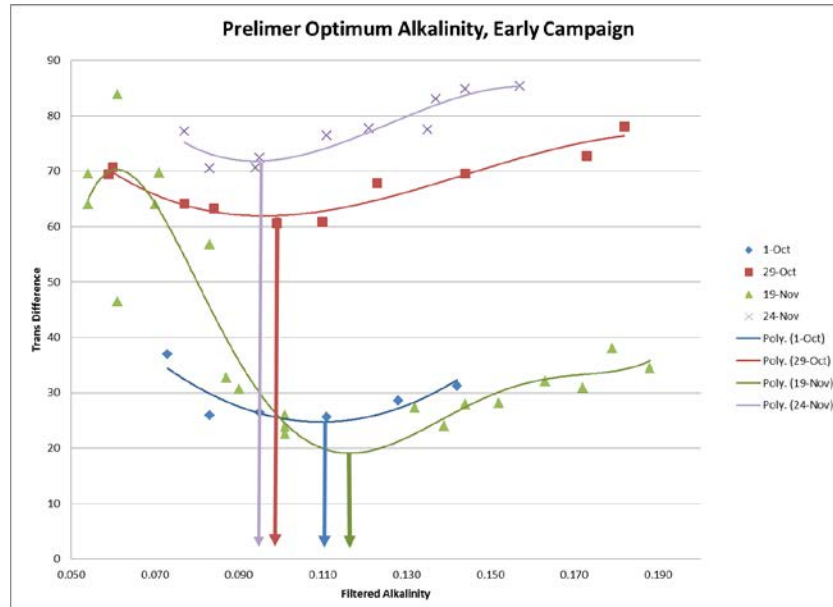


Figure 7

The daily average final pre-limer filtered alkalinity and the 1st carb filtered alkalinity for this period are shown in Figure 8. Note the near convergence of the filtered alkalinity of the pre-limed juice and that of the filtered alkalinity of 1st carbonation. Purification non-sugar elimination averaged 26.2% with total elimination relative to cossette purity averaging 44.0%

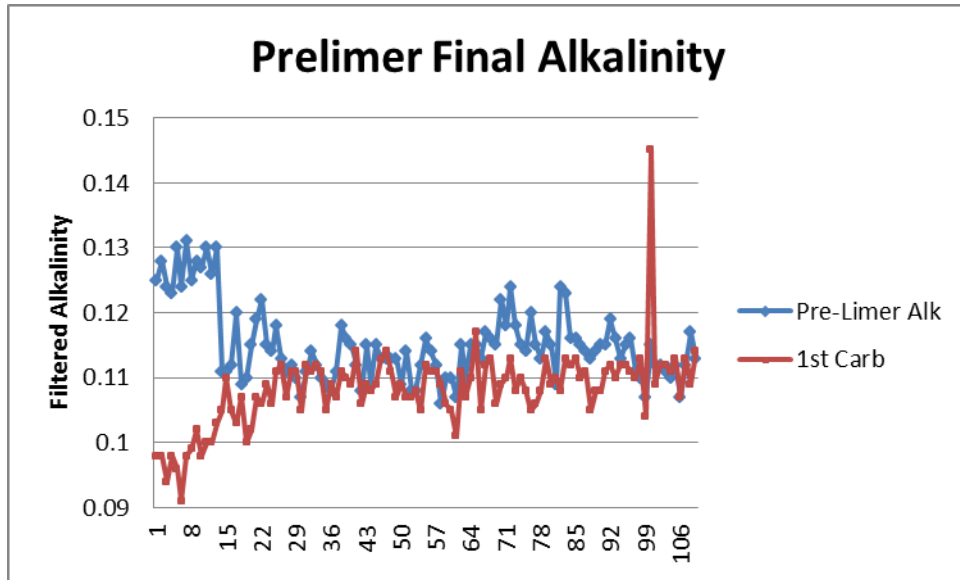


Figure 8

As the campaign proceeded and beet quality began to deteriorate, the optimum end point determination began to exhibit an interesting variation in that the end point appeared to spread over a larger alkalinity range rather than at a clear minimum in the difference in transmittance between the filtered and unfiltered samples obtained in the optimum alkalinity determination. These late campaign determinations are shown in Figure 9.

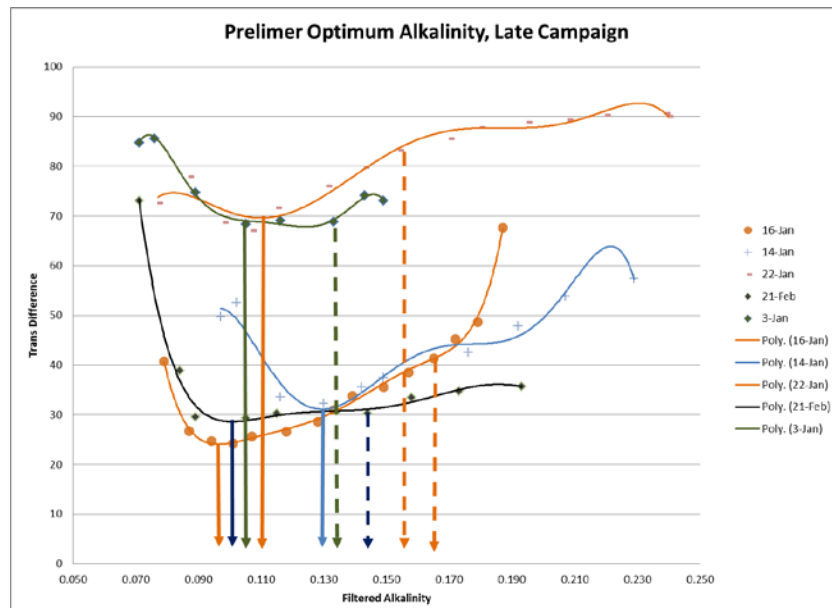


Figure 9

With one exception, the optimum end point alkalinity at the beginning of the minimum difference in transmittance was observed to be at only a slightly lower target alkalinity than with the early campaign beets. However, very difficult 1st Carb mud filtration properties were

encountered when operating in this alkalinity range. It was discovered that it was necessary to operate at a final pre-liming alkalinity somewhat higher, as represented by the dashed lines on the chart in Figure 9, to achieve reasonably satisfactory 1st Carb mud filtration characteristics. The actual pre-liming final alkalinity at which the factory was operated is shown in Figure 10.

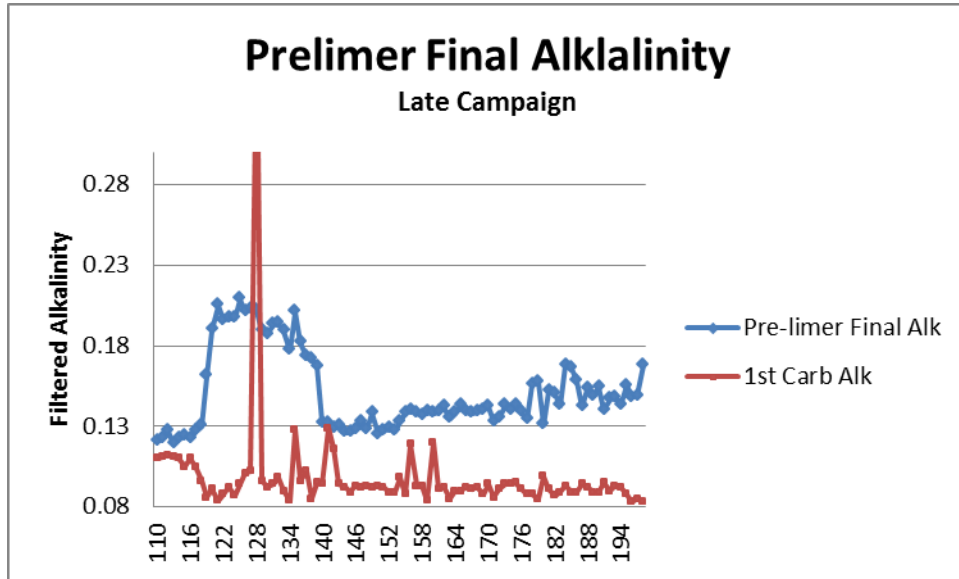


Figure 10

It should be noted that very difficult operating conditions were encountered during this period than is normally delivered to the factory for processing. Thus, the required shift in final pre-liming alkalinity noted may not be representative of typical late season operating conditions. In spite of the beet quality situation, the factory was able to average 25.2% non-sugar elimination in purification and 35% total non-sugar elimination relative to cossette purity on a mixture of freeze/thaw damaged beets and otherwise abnormally warm storage conditions.

Summary

Procedures noted herein will result in optimal pre-limer control and performance. Through the application of the procedures and control methods noted, it is possible to maintain relatively optimal pre-liming performance over a relatively wide range of operating conditions and beet quality. Certain severe adverse conditions affecting 1st Carb mud filtration performance may require somewhat higher final pre-liming alkalinity than indicated by the test for determination of the optimum endpoint. Such conditions may be indicated by an abnormal flattening of the minimum point of the optimum alkalinity determination plot of transmittance difference between filtered and unfiltered sample aliquots.

References

1. Kraus, W.; Stark T.; Rad M. A.; Mauch W. (1997): Investigations of conditions for optimum colloid coagulation in prelining of beet juice. Zuckerind. 122 (1197) Nr. 2, S. 91-99
2. Putsch GmbH & Co. KG: The juice purification. E-mail: info@putsch.com

Appendix 1: Stepwise Procedure for the Determination of Optimum Pre-limer Final pH (Alkalinity)¹

In this procedure, a relatively large sample of raw juice is collected from process and while being maintained at the process pre-liming temperature the sample pH is incrementally increased to 11.8 over a period of about 20 minutes.

1. Collect approximately 2 liter of raw juice from process in a suitable container and maintain the temperature of the sample during the test to that of the processing temperature with constant stirring of the sample.
2. Progressively add approximately 4 ml of MOL to the sample at a minimum of 1 minute intervals.
3. Take a 20-25 ml sample from the solution just prior to each addition of MOL and place in a test tube. Note whether or not flocculation is present. If flocculation is not present, return the sample to the 2 liter test sample and add the next 4 ml aliquot of MOL to the container holding the sample solution.
4. If there is flocculation present, place the 20-25 ml sample in the test tube in a test tube holder placed in a 20⁰C water bath and then add the next 4 ml aliquot of MOL to the test sample.
5. Continue collecting samples in this manner until the pH of the test solution is 11.8. Approximately 15 to 20 individual samples should have been collected. (See Figure 1.)

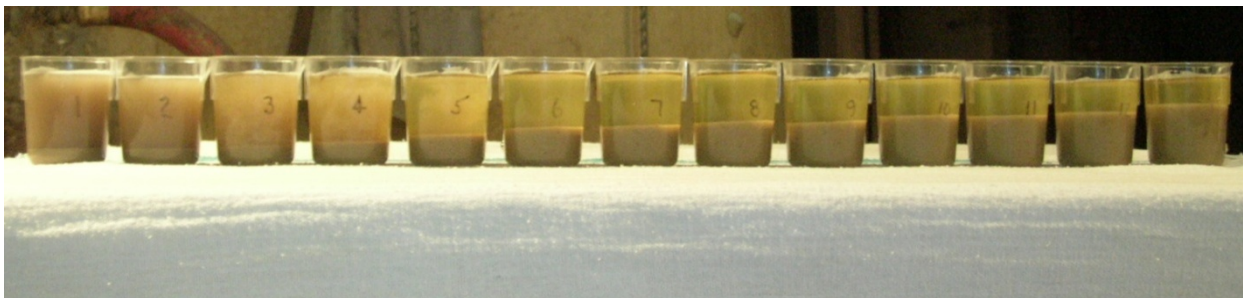


Figure 1

6. Allow the samples to set in a 20⁰C water bath for approximately 1 hour to allow for complete settling of flocculated particles. Note that there will still be turbidity in some of the sample while others will appear relatively clear above the precipitate.
7. Pipette 3 ml of the supernatant liquid from each test tube to a 10mm path length cuvette and measure the transmittance of each sample at 530 nm. Record each of these values numbered “1” through the highest sample #. When complete, return each sample to its respective test tube.
8. Filter a portion of the filtrate from each test tube through a 0.45um filter and place 3 ml of the filtered supernatant solution in a 10 mm path length cuvette. Measure and record the absorbance value for each of these samples numbered “1” through the highest sample

- #. When complete, return each sample to its respective test tube along with any unused filtered portion.
9. Analyze each test tube sample for pH and alkalinity. (All alkalinity samples should be filtered through regular filter paper prior to analysis. It may be advisable to collect a second duplicate sample for the determination of pH and alkalinity at the same time the test tube samples are taken.)
 10. Plot the difference between the absorbance of the unfiltered versus the filtered samples against pH (and alkalinity). The optimum pH (alkalinity) is the point at which there is a minimum difference between the two values. (See Figure 2.)

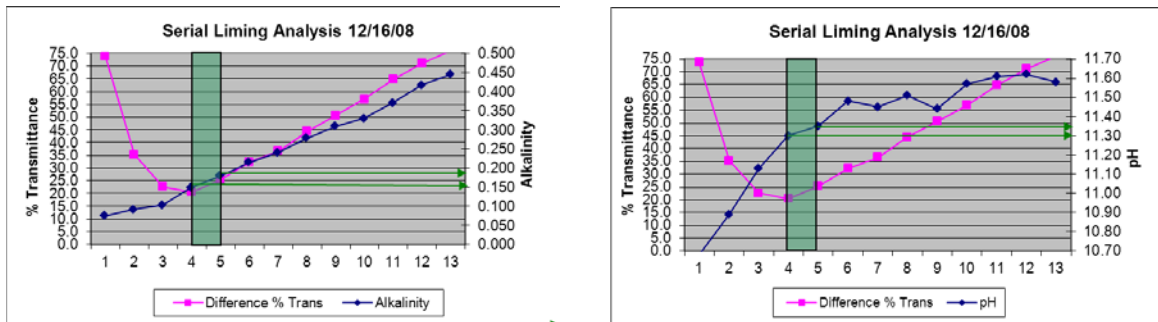


Figure 2

Appendix 2: Pre-limer pH (Alkalinity) End-Point Optimization - Quick Test

List of Materials:

1. 5 gallon Bucket
2. 50 mL scoop/ladle
3. 2 dozen 250 mL clear beakers
4. 25 micron filter paper
5. Phenolphthalein pH indicator solution
6. 50 mL graduated burette
7. Latex or Nitrile gloves
8. ½ gallon Jug
9. 250 mL scoop/ladle
10. pH meter
11. Filtration funnel
12. 0.0357 N H₂SO₄ solution
13. Safety glasses
14. Long sleeved shirt or lab coat

Procedure:

1. Obtain approximately 4 gallons of juice in a 5 gallon bucket from the prelimer cell where 1st Carb sludge is returned.
2. Obtain approximately half a gallon of factory Milk Of Lime (MOL) in an appropriate container and keep well mixed during the procedure
3. Using the 250 mL scoop, take a 150 mL sample from the bucket and set it aside in a 250 mL beaker
4. Add 50 mL of MOL to the bucket using the 50 mL scoop and thoroughly stir with the 250 mL scoop for about 1 minute.
5. Take another 150 mL sample and set aside in a beaker
6. Repeat steps 4 and 5 until the pH in the bucket reaches 12.0 pH
7. Line up all of the sample beakers in sample order with sufficient lighting behind the samples to verify sample clarity
8. Visually select a 3-4 sample group exhibiting the highest level of clarity from the line of samples and set aside
9. Filter each of the separated samples through a 25 micron filter paper
10. Titrate 10 mL of each **filtered** sample with 0.0357 N H₂SO₄ from a 50 mL graduated burette to a phenolphthalein end point
11. Convert the number of milliliters of H₂SO₄ used to alkalinity by using the following equation:
 - $(\text{mL H}_2\text{SO}_4) * (1/10) = \text{Alkalinity (report to 3 decimal points: x.xxx)}$
12. The operating target range for Pre-limer final **filtered** alkalinity is the alkalinity range determined by the 3-4 sample group